PB82-114224

Application of the Empirical Kinetic Modeling Approach to Urban Areas. Volume II: Tulsa

Systems Applications, Inc.
San Rafael, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

May 81

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-114224

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-81-005b
May 1981

Air

EPA

Application Of The Empirical Kinetic Modeling Approach To Urban Areas

Volume II: Tulsa

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
2.
3. RECIPIENT'S ACCESSION NO. PB82 114224
4. TITLE AND SUBTITLE
Application of the Empirical Kinetic Approach (EKMA) to the Tulsa Area
5. REPORT DATE
6. PERFORMING ORGANIZATION CODE U282023
7. AUTHOR(S)
H. Hogo, G. Z. Whitten, and S. D. Reynolds
8. PERFORMING ORGANIZATION REPORT NO.
49r-81-EF81-116
9. PERFORMING ORGANIZATION NAME AND ADDRESS

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, California 94903

10. PROGRAM ELEMENT NO.
11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS

Air Management Technology Branch
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES
Gerald L. Gipson

16. ABSTRACT

The EKMA was evaluated using applications in the Tulsa area primarily by comparing the trajectory model that forms the basis of the EKMA (OZIPP) with other, more sophisticated, models. The study was carried out at several levels, beginning with evaluation of OZIPP and ending with an evaluation of the control-strategy predictions that result from employing the EKMA isopleth methodology. The OZIPP trajectory model was compared with the SAI Airshed Model and the SAI trajectory model, as well as with some modified versions of the original OZIPP model.

The basic OZIPP model is a simple, moving-air parcel, or trajectory, model that uses a detailed chemical mechanism for the surrogate propylene and butane hydrocarbons. The model treats time-dependent, precursor-emission factors along with expansion of the air parcel; entrainment is treated by assuming that constant concentrations exist outside the parcel.

The primary emphasis of this comparison study was directed toward the discovery of features in the basic OZIPP model that could explain differences in the results of the OZIPP model from those of some other model.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Control Strategies Photochemical Pollutants Models EKMA OZIPP		

18. DISTRIBUTION STATEMENT
19. SECURITY CLASS (This Report)
20. SECURITY CLASS (This page)
21. NO. OF PAGES 190
22. PRICE

EPA Form 2220-1 (9-73)

EPA-450/4-81-005b

Application Of The Empirical Kinetic Modeling Approach To Urban Areas

Volume II: Tulsa

by

G.Z. Whitten and H. Hogo

Systems Applications, Incorporated
950 Northgate Drive
San Rafael, California 94903

Contract No. 68-02-3376

EPA Project Officer: Gerald L. Gipson

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

May 1981

DISCLAIMER

This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The EKMA was evaluated using applications in the Tulsa area primarily by comparing the trajectory model that forms the basis of the EKMA (OZIPP) with other, more sophisticated, models. The study was carried out at several levels, beginning with evaluation of OZIPP and ending with an evaluation of the control-strategy predictions that result from employing the EKMA isopleth methodology. The OZIPP trajectory model was compared with the SAI Airshed Model and the SAI trajectory model, as well as with some modified versions of the original OZIPP model.

The basic OZIPP model is a simple, moving-air parcel, or trajectory, model that uses a detailed chemical mechanism for the surrogate propylene and butane hydrocarbons. The model treats time-dependent, precursor-emission factors along with expansion of the air parcel; entrainment is treated by assuming that constant concentrations exist outside the parcel.

The primary emphasis of this comparison study was directed toward the discovery of features in the basic OZIPP model that could explain differences in the results of the OZIPP model from those of some other model.

CONTENTS

Disclaimer.. ii
Abstract.. iii
Figures... v
Tables.. vi

1. Introduction... 1
    Background and objectives....................................... 1
    The empirical kinetic modeling approach......................... 2
    An overview of EKMA comparison evaluations...................... 3
2. Summary, Conclusions, and Recommendations........................ 5
    Summary... 5
    Conclusions... 5
    Recommendations... 9
3. Model Applications... 14
    Definition of the models.. 15
    Description of the Tulsa modeling region........................ 23
    Characterization of the Tulsa modeling days..................... 23
    Inputs used in the SAI Airshed Model simulations................ 29
    Inputs used in the SAI trajectory model simulations............. 30
    Inputs used in the Level II CBM/OZIPM and Level II OZIPM model simulations.................................... 40
    Inputs used in the Level III EKMA model simulations............. 49
4. Comparison of Model Results...................................... 60
    SAI Airshed Model results....................................... 60
    Comparison of SAI Airshed and SAI trajectory model results...... 65
    Comparison of SAI trajectory and Level II EKMA model results.... 68
    Level III EKMA model results.................................... 78
5. EKMA Isopleth Calculations....................................... 92
6. Sensitivity Studies.. 112
    Sensitivity of the EKMA Model to emissions density information.. 112
    Sensitivity of the propylene/butane chemistry due to variation in rate constants................................... 114
    Sensitivity of models to hydrocarbon and NO_x background concentrations.. 118
    Sensitivity of Level II EKMA models to trajectory selection involving wind shear... 127

References.. 132
Appendix: Description of Inputs Used in SAI Airshed Model Simulations... 134

FIGURES

Number Page

3-1 The gridded Tulsa modeling region.......................... 24

3-2 Initial conditions in the ground-level grid cells on 3 August 1977 (isopleths in increments of 2 pphm)........ 31

3-3 Initial conditions in the ground-level grid cells on 21 July 1977.. 33

3-4 The diurnal pattern of the mixing depth and top of the modeling region... 36

3-5 Trajectory path (CDT)...................................... 41

3-6 Level III straight-line trajectory to maximum O_3........... 51

4-1 Comparison of NO_x, PAR, ETH, BZA, PAN, and ozone for the SAI trajectory and CBM/OZIPM models for 29 July 1977..... 71

4-2 Comparison between station-observed ozone and CBM/OZIPM predictions.................................... 74

4-3 Level II EKMA trajectory for Tulsa, Oklahoma............... 80

4-4 Level III EKMA trajectory for Tulsa, Oklahoma.............. 84

4-5 Level III EKMA trajectory for Tulsa, Oklahoma, using the Carbon-Bond Mechanism.............................. 88

5-1 Level III trajectory for Tulsa, Oklahoma.................. 97

5-2 Level III trajectory for Tulsa, Oklahoma, using the Carbon-Bond Mechanism.................................... 103

6-1 Trajectory paths used in the EKMA sensitivity study of grid resolution for 21 July 1977......................... 113

6-2 CBM/EKMA Oklahoma simulation of 20 July 1987--trajectory to the regional ozone maximum 119

6-3 Typical transport flight pattern............................ 128

6-4 Comparison of trajectory paths based on two different wind patterns for 29 July 1977............................ 130

6-5 Total ground-level emissions of hydrocarbons for the Tulsa region in kg/hr between the hours of 0800 and 0900 (CDT).. 131

TABLES

Number Page

3-1 Maximum Observed Ozone Concentration for the Four Modeling Days in 1977 25

3-2 Boundary Concentrations Used in the Tulsa Simulations (ppm) 35

3-3 Initial Conditions and Emissions Rates Used in the Level II CBM/OZIPM Calculations for 21 July 1977 45

3-4 Initial Conditions and Emissions Rates Used in the CBM/OZIPM Calculations for 29 July 1977 46

3-5 Initial Conditions and Emissions Rates Used in the CBM/OZIPM Calculations for 3 August 1977 47

3-6 Initial Conditions and Emissions Rates Used in the CBM/OZIPM Calculations for 2 September 1977 48

3-7 County-wide Emissions Estimates for 1977 50

3-8 Calculated Emissions Density for Five Oklahoma Cities 50

3-9 Initial Conditions Used in the Level III EKMA Calculations for 21 July 1977 55

3-10 Initial Conditions Used in the Level III EKMA Calculations for 29 July 1977 56

3-11 Initial Conditions Used in the Level III EKMA Calculations for 3 August 1977 57

3-12 Initial Conditions Used in the Level III EKMA Calculations for 2 September 1977 58

4-1 Comparison of Ozone Predictions for the SAI Airshed, SAI Trajectory, Level II, and Level III EKMA Models--1977 61

4-2 Summary of Peak Ozone Concentration Model Performance Evaluation Measures 62

4-3 Summary of SAI Airshed Model Performance Evaluation Measures 66

4-4 Aloft Concentrations of BZA and PAN Used in the SAI Trajectory Model and the CBM/OZIPM Model 70

4-5 Comparison of SAI Trajectory and the CBM/OZIPM Model Ozone Prediction 79

5-1 Emission Inventory Summary for the Tulsa Study Area 93

5-2 Control Strategies to Be Used in the Tulsa Modeling Study 94

5-3 Ozone Predictions from EKMA Model Single-Day Diagrams (ppm) 95

5-4 Ozone Predictions from Various Models for the Tulsa Modeling Days (lowered ozone aloft in the EKMA models) (ppm) 109

5-5 Required Percentage Reductions in Hydrocarbon Predicted by the EKMA to Reach 0.12 (ppm) Ozone Levels (3.7 percent NO_x reduction assumed) 110

6-1 Emissions Rates for Trajectories Parallel to the One to Vera for 21 July 1977 115

6-2 Initial Conditions Used in the EKMA Calculations for 21 July 1977 116

6-3 Level II EKMA Ozone Predictions Using the Propylene/Butane Chemistry for 21 July 1977 under Various Conditions (observed ozone = 0.14 ppm) 117

6-4 SAI Trajectory Model Results Obtained by Varying Hydrocarbon and NO_x Concentrations in the Surface and Aloft Layers 122

6-5 Effect of Precursor Conditions on Ozone Predictions for 29 July 1977 for the CBM/OZIPM and Level III EKMA Models........ 124

6-6 Calculation of Contribution Factors of Transported Pollutants to Urban Levels--1977........ 125

6-7 Aircraft Measurements of NMOC........ 126

1 INTRODUCTION

BACKGROUND AND OBJECTIVES

For several years the Office of Research and Development of the EPA has sponsored a coordinated program consisting of fundamental chemical research, smog chamber experimentation, and model development. The objective of this program is to develop mathematical models capable of simulating the dynamics of the chemical reactions and dispersion of the gaseous pollutants found in the lower troposphere. These atmospheric models are to be used both to gain an understanding of air pollution and to predict the probable outcome of control scenarios. To this end, the EPA Office of Air Quality Planning and Standards (OAQPS) has embarked on an extensive program of model comparison and evaluation.

The specific purpose of the OAQPS program is to assess the suitability of available photochemical oxidant modeling approaches for use by states as planning tools in ozone air quality planning and management. The program includes comparisons and evaluations of the various approaches for typical U.S. cities. As part of the program, large, detailed data bases are being assembled for several example cities.

The primary objective of this study is to evaluate one such approach--the EKMA--through the application of the photochemical trajectory model (OZIPP) that forms its basis. The EPA has prepared highly detailed data concerning precursor emissions, meteorology, and ambient air quality for Tulsa and Philadelphia to test various air quality simulation models such as the OZIPP and the SAI Urban Airshed Model. In addition, there are data bases already available for St. Louis, Los Angeles, San Francisco, and Sacramento. Because some models are grid-based and thus designed to reproduce spatial and temporal variations within the metropolitan airshed, detailed information files are required. The availability of detailed data and of the results from parallel studies using sophisticated models offers the following advantages for making an in-depth study of the EKMA:

- The simple application of the OZIPP trajectory model, using either the actual available data inputs or the corresponding data simulated in other models, should generate results that can be compared both with ambient air data and with the results of the other models. The timing of results regarding data such as the ozone maxima and precursor decay should also be comparable.
- Tests of the sensitivity of the results to variations in the input data can demonstrate important data requirements for successful application of OZIPP. This information should be useful in determining cost effectiveness for future uses. The results of the sensitivity study are also useful for improving the trajectory model in case the present version does not adequately simulate observed ambient data or the simulations of more complex models.
- The application of the EKMA procedures to air quality planning demonstrates the utility of the EKMA compared with that of methods based either on simpler models or on more complex models (such as the SAI Urban Airshed Model).
- The potential effectiveness of OZIPP model improvements can be assessed using the results of the complex models as a standard.

THE EMPIRICAL KINETIC MODELING APPROACH

The Environmental Protection Agency (EPA) has developed a method for estimating the emission controls that will be needed to meet the National Ambient Air Quality Standard (NAAQS) for ozone (O_3) concentrations in urban areas. This method, known as the Empirical Kinetic Modeling Approach (EKMA), uses an isopleth diagram of ozone concentrations that is related to hydrocarbon (HC) and nitrogen oxide (NO_x) precursor levels. Each point on the isopleth diagram represents the maximum one-hour ozone level reached as a result of the specific HC and NO_x combination described by the abscissa and ordinate values of the isopleth diagram. The ozone value generated from each HC and NO_x combination is obtained by means of a computer-based trajectory model--the Ozone Isopleth Plotting Package (OZIPP) (Whitten and Hogo, 1978a). The OZIPP trajectory model contains many simplifying assumptions and options that are designed to strike a balance between factors such as the state of knowledge, data availability, computer size, predictive accuracy, and overall cost.

AN OVERVIEW OF EKMA COMPARISON EVALUATIONS

This is the third of four studies performed at SAI to evaluate the EKMA through comparison of the OZIPP trajectory model with other models. The first study compared the SAI grid and trajectory models with various versions of the trajectory model used in the EKMA for the Los Angeles area (Whitten and Hogo, 1981); the second study involved two cities and two grid models: The LIRAQ model formed the basis for the San Francisco area comparison; for the Sacramento area the SAI model was used again (Whitten, Hogo, and Johnson, 1981). The SAI model was also used for the present study of the Tulsa area.

A comparison evaluation is done at several levels that provide a spectrum of information. The independent application of the EKMA-OZIPP in areas where other models have been applied merely validates the common assumption that different models can sometimes produce different results. This study attempts to go farther and to provide information explaining why specific features of the different models lead to different results. For instance, a specific feature of grid models, in contrast to trajectory models in general, is their ability to simulate some wind shear effects. The two models (grid and trajectory) have been found to produce different results when wind shear effects are significant; the reverse is also true (similar results can occur when wind shear is minimal). Thus, specific differences in models can be associated with differences in their results. Given the previous example, a prospective user would do well to apply the trajectory model with a measure of discretion in a situation known to have a high wind shear.

Different levels of evaluation are possible within the framework of the EKMA. The control scenario estimations generated by the use of EKMA isopleth diagrams are the end result of a series of steps involving model assumptions and adjustments. At the beginning or base of the EKMA is a trajectory model that is basically quite simple from the standpoint of dispersion. This trajectory model can be applied in the absolute sense as an atmospheric model on its own. The OZIPP computer code that contains this model also has an array of options, each of which will be geared to some specific standardized setting if the user does not exercise the option.

The isopleth diagram is used in a relative manner so that, if all the options and inputs fail to generate a simulated ozone value that agrees with observations, the final discrepancy is eliminated by using the observed value. Some discrepancy is almost always expected because, except for the chemistry employed, the EKMA-OZIPP is a rather simplistic approach. The use of the observed ozone value rather than the simulated value is intended to account for some of the simplifications inherent in the EKMA-OZIPP.

The levels of evaluation in this study begin with the specific features that define each basic model; other levels involve input data, options, and, eventually, the methodology of constructing and using the isopleth diagrams. At each level, the present study attempts to make comparisons with other models, observations, and alternate methodologies. However, like many situations in nature, the evaluation of atmospheric models does not necessarily fit a specific, well-organized framework. Problems that are unique to some areas are not always apparent ahead of time. Thus, this present study, which uses data from the Tulsa area, is only part of an overall evaluation of the EKMA. Following sections present the specific results and analysis of the Tulsa study as they relate to the EKMA evaluation.

2 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

We have evaluated the EKMA primarily by comparing the trajectory model that forms the basis of the EKMA (OZIPP) with other more sophisticated models in applications to the Tulsa area. The study was actually carried out at several levels, beginning with evaluation of OZIPP and ending with an evaluation of the control-strategy predictions that result from employing the EKMA isopleth methodology. The OZIPP trajectory model was compared with the SAI Airshed Model and the SAI trajectory model, as well as with some modified versions of the original OZIPP model.

The basic OZIPP model is a simple, moving-air-parcel, or trajectory, model that uses a detailed chemical mechanism for the surrogate propylene and butane hydrocarbons. The model treats time-dependent, precursor-emission factors along with expansion of the air parcel; entrainment is treated by assuming that constant concentrations exist outside the parcel.

CONCLUSIONS

The primary emphasis of this comparison study was directed toward the discovery of features in the basic OZIPP model that could explain differences in the results of the OZIPP model from those of some other model. To that end, most of the OZIPP simulations utilized initial conditions derived from the model used for comparison purposes. Thus, for the most part, the study used the SAI Airshed Model data files to generate appropriate OZIPP inputs. Although the utilization of these files tends to circumvent the issue of normal-source data preparation, the comparison of models is clarified by use of common data bases. Furthermore, costs are minimized. For some of the OZIPP simulations, we used air quality data rather than information common to the comparison model. This step allowed the categorization of overall differences as either effects resulting from the data utilized or those attributable to specific features of the models.

This study, and similar studies by Whitten and Hogo (1981) and Whitten, Hogo, and Johnson (1981) using Los Angeles, San Francisco, and

Sacramento data, show that the OZIPP model can provide results that are often quite similar to those of the more complex models. By carefully separating the models according to specific formulation differences and through careful analysis of intermediate results, the most important feature in formulation that produced the difference in the results of two models could often be isolated. Even though the absolute values predicted by the OZIPP trajectory model can be significantly different from those of the more complex models (one difference can result from the different chemical mechanisms employed), the isopleth applications of the EKMA (which uses the trajectory model results in a relative fashion) typically show control predictions that correspond with those of the more complex models.

The present study differs from the previous evaluations in that the EKMA and Airshed Models were evaluated simultaneously instead of the EKMA evaluation following that of the Airshed Model. This timing allowed a certain interchange and feedback between the two studies:

> Isopleth diagrams were constructed to assist the development of control scenarios for the SAI Airshed Model study. The original diagrams showed quite clearly that the background hydrocarbon levels used in the Airshed Model study significantly affected the results of potential control requirements. Therefore, the original estimates of background hydrocarbons were reevaluated and were found to be erroneously high. The subsequent lowering of the estimates led to an additional base case validation of the Airshed Model.

> One of the modeled days (29 July 1977) was characterized by significant wind shear within the mixed layer. The trajectory models could not produce results similar to those of the Airshed Model, even when an average value for the winds was used to define a trajectory path. The sensitivity to trajectory path (due to the divergent emissions patterns) was so great in this study, however, that even the grid model may be inadequate. The version of the grid model used in this study had only two model layers within the mixed layer. Adequate simulation may require more than two layers to account for the combination of significant wind shear and highly divergent emissions patterns.

The main conclusions reached in this study from comparison of the grid and trajectory models in application to the Tulsa area are similar to those of previous studies such as Whitten, Hogo, and Johnson (1981):

- These two basic types of models tend to show close agreement only in the absence of wind shear.

- Any trajectory model, when run in conjunction with a grid-model study, can serve as a useful and inexpensive tool for understanding, analyzing, and testing important and sensitive elements of the situation being modeled.

- The SAI trajectory model serves as a source of data for the EKMA models, as well as an important conceptual link between these models and the SAI Airshed Model.

Comparisons of the SAI trajectory model and an EKMA model (CBM/OZIPM) modified to most closely resemble the SAI trajectory model showed that many features in the SAI trajectory model can often be eliminated or simplified with a minimal effect on results. For instance, the two levels within the mixed layer of the SAI trajectory model seem adequately represented by a single layer in the CBM/OZIPM model. The same photochemical kinetic mechanism, the Carbon-Bond Mechanism, is used in the SAI Airshed Model, the SAI trajectory model, and the CBM/OZIPM model. This mechanism is described as CBM-II by Whitten, Killus, and Hogo (1980).

Two important differences in model characterization were identifed in this study, however:

- Surface deposition, neglected in the EKMA models, can reduce ozone values by as much as 15 percent.

- Entrainment of PAN and reactive intermediate compounds from aloft can increase ozone by as much as 10 percent.

The EKMA models normally entrain only O_3, NO_2, and hydrocarbons from aloft and the concentrations aloft are assumed to be constant during the day, whereas more sophisticated trajectory models, such as the SAI trajectory model used in this study, simulate the same species aloft as in the mixed layer, and the time-dependent chemistry aloft is simulated as well. There were no measurements of PAN or other reactive intermediates aloft. However, the SAI multilayer models (the Airshed Model and the trajectory model) do simulate concentrations of these species aloft and subsequently entrain them into the mixed layer when the inversion height rises. Modification of an EKMA-type model to entrain the same amounts of these species as are simulated aloft in the SAI model resulted in up to a 10 percent increase in ozone.

The single substitution of the CBM chemistry for the standard EKMA propylene/butane chemistry produced a modified EKMA model that could be used with the standard EKMA to compare the two chemistries. This substitution showed that the propylene/butane mechanism frequently generated less ozone than did the CBM. This reduced ozone generation was found to be a result of some outdated rate constants; the key type of reaction involved the conversion of NO to NO_2 via peroxy radicals (RO_2 and HO_2).

For the 1982 SIP studies the EPA has designated degrees of model sophistication by Levels I through IV, which are described on pages 65669-65670 in the November 14, 1979, Federal Register. In this study Level I models are the SAI Airshed Model and the SAI trajectory model. Versions of the OZIPP trajectory model used in this study, which use trajectory paths derived from wind measurements, are considered to be Level II EKMA. The important feature defining a Level III EKMA model is the assumed trajectory relating early morning urban precursors to an observed ozone peak (EPA, 1980, October draft).

Level III EKMA simulations that showed reasonable agreement with observations were also performed, though the simulated values were low, in general. However, the use of county-wide emissions in this model makes detailed comparisons with the other models used in this study difficult because the emissions data are different.

The CBM was also substituted for the regular propylene/butane chemistry in the Level III EKMA model. The ozone levels generated by the CBM in this test were, in general, higher than the simulated ozone levels generated by the propylene/butane chemistry. Both the CBM and the propylene/butane mechanism were used with their respective default reactivities. Use of the CBM with reactivities suggested by the Tulsa emissions data resulted in the generation of rather low ozone levels. A reevaluation of the Tulsa emissions data is in progress. Preliminary results to date indicate reactivities approaching the CBM default level.

Those conclusions based on comparisons of control scenario predictions for the SAI Airshed Model and the EKMA isopleths were, unfortunately, limited by time constraints. At the time of this writing, only one base case day (29 July 1977) had been used for control simulations in the grid model study using a 1987 emissions inventory with several options. For this comparison, Level III EKMA isopleth predictions tended to be quite close to the SAI Airshed Model predictions. Unexpectedly, the substitution of the CBM into Level III EKMA isopleths resulted in significantly lower ozone predictions for 1987. The reasons for this effect are complex and require further study.

Those conclusions of the present study specific to the sensitivity of various parts of the EKMA were as follows:

> Emissions density information--Although adjacent Level II trajectory paths produced significantly different results because of different emissions densities, the use of broader trajectory paths with averaged emissions eliminated this sensitivity.

> Rate constant adjustments in the propylene/butane mechanism--Although many rate constants have now become somewhat out of date, a critical rate involving peroxy radical reactions with NO was identified. Moreover, the ratio of this type of rate to the formation of nitric acid from NO_2 was shown to be important.

> Surface and aloft precursors in the background air--These were shown to play a critical role in the Airshed Model study of the Tulsa area. Control strategy implications were found to be highly sensitive to the overstated values assumed for precursor levels in future background air.

> Trajectory path determination with wind shear--Attempts to use average wind direction under wind shear conditions demonstrated the importance of path determination over widely varying emissions patterns for Level II models.

RECOMMENDATIONS

The following considerations are suggested for future studies:

> For cases in which differences in control strategy predictions are found to be related to differences in the chemistry employed in various models, it is important to investigate the chemical reactions that produce these differences. If appropriate smog chamber experiments that would validate one or more types of mechanisms can be identified, these experiments should be performed.

> The use of more complex models such as the SAI Airshed Model should be accompanied by the use of the EKMA, both for absolute trajectory simulations along the path to the major ozone peaks and for control strategy guidance from the isopleth diagrams. The studies performed to date show

that unless the wind fields are complicated by such factors as wind shear, the two types of models normally give similar results. In the absence of complex meteorological factors, important differences in results would indicate the existence of problems in one or both of the models that should be investigated.

> Identification of background concentrations and reactivities must be carefully considered for both present and future simulations. Severe control requirements can be implied if the level of background pollutants is overstated.

> The regular city-specific algorithm might be modified to allow optional starting times in place of the present 0800 LDT starting time. Earlier starting times would emphasize dependence on an emissions inventory, whereas later starting times might emphasize dependence on initial conditions.

> Modifications to the current version of the EKMA have also been suggested in other studies. Although such suggestions have not been addressed in this study, their implementation might also be considered.

  - The two-stage approach (in which stationary-source emissions are held constant in the first stage and mobile-source emissions are held constant in the second stage) might be further developed so that local districts can use EKMA isopleths to make the control predictions for stationary emissions.

  - Isopleths based on emissions inventories might be further developed to perhaps replace the present initial-condition-based isopleths. Urban HC and NO_x measurements are often not relevant to the initial trajectory. Trajectories might originate prior to the present time of 0800 hours. Path definition is not important to moving-air-parcel models in general, unless differences in emissions density and mixing height exist. Preliminary calculations suggest that precise definition of mixing height prior to 0800 hours is unimportant. Wind velocities prior to 0800 hours are typically low so that few grid squares would be crossed before the arrival of the wind at the more easily definable trajectory paths now used, those beginning at 0800 hours. Therefore, an important factor in the success of an emissions-dominated model would be minimal, or at least moderate, diversity of the emissions density in the vicinity of the present 0800 starting area. To be sure, the present study identifies the sensitivity to emissions diversity for path definition in connection with attempts to simulate a day exhibiting wind shear (see section 6). A probable solution to that case would have been an averaging of the emissions across several grid squares upwind of the 0800 location of the main trajectory path.

An emissions-oriented model is also potentially more advantageous than the present initial-condition-and-measured-HC/NO_x model because of the poor mixing that can occur prior to 0800. Measured urban HC and NO_x values often vary widely even when taken at the same location as a result of local mixing and local emissions. Using the HC/NO_x ratio does not necessarily mitigate the problem because the measured ratios can still be dominated by local emissions and mixing effects. Starting the model earlier and filling it with well-mixed emissions from the region upwind of, and within, the main urban area provides a more realistic simulation of the air that arrives at the downwind site where the ozone maximum occurs. Furthermore, the ordinate and abscissa (which are scaled relative to the emissions rather than initial concentrations) would relate more closely to the purpose of the EKMA (i.e., to estimate the changes in peak ozone resulting from changes in emissions).

- The mixing-depth algorithm should be improved so that the changes with time correspond to observations instead of producing a constant-dilution factor.

- The transported pollutants, both in the surface layer and aloft, might be varied by the user. The range of variance would be between present levels and some minimal natural background level. For some cities, there is evidence to suggest that air transported into the area is actually returning from a previous day. Other cities may be downwind of another urban area that requires similar controls. The current procedure requires two separate isopleth diagrams. (Again, further development would be necessary to incorporate this refinement.)

- The use of atmospheric models under conditions of wind shear within the mixed layer should be approached with caution. Although Level II trajectory models are basically inappropriate under such conditions, their use to assess a specific area can still be helpful in Level I grid model studies.

- A generic concept can be associated with the EKMA that goes beyond its present formulation and uses. Developmental work on the EKMA should be continued to update its formulation and improve its utility. Specifically, the following steps are suggested:

  - This study demonstrates that significant differences in both absolute model results and in predicted control requirements can sometimes occur when the Carbon-Bond Mechanism is substituted for the propylene/butane chemistry currently used in OZIPP. Further studies should be undertaken to investigate and resolve potential discrepancies between the two mechanisms.

  - Point source emissions might be handled so that the interaction with all possible urban HC/NO_x concentrations could be evaluated as part of a new-source review procedure.

  - Percent cutback diagrams (PCD) might be added to the OZIPP code so that both the isopleth and the PCD are generated.

  - Temperature changes, deposition, variable reactivities, nitrate chemistry, and sulfate chemistry can be added to the OZIPP. Isopleths of species other than ozone can also be generated by OZIPP.

  - Statistical packages can be combined with the EKMA to generate the probable number of exceedances resulting from various control scenarios.

- Credibility of the EKMA could be enhanced by providing a means for considering urban hydrocarbon reactivity. Either the latter should be related to the proplyene reactivity used in OZIPP, or the chemical mechanism utilized in the OZIPP should be changed to be compatible with available reactivity information.

49r 81 21

SECTION 3

MODEL APPLICATIONS

This section describes the different photochemical air quality models used for this study and the inputs associated with each model. Descriptions of the Tulsa study region and the modeling days used in that study are also presented in this section.

The purpose of this study is to compare ozone predictions between air quality models of different complexity (in particular, to perform EKMA calculations along with current SAI Airshed Model applications). These models can be classified, on the basis of their complexity, according to the levels of analysis described in the 1980 Federal Register notice on ozone modeling:

> SAI Airshed Model--Level I analysis using a complex grid model.

> SAI trajectory model--Level I analysis using a complex trajectory model.

> OZIPM/CBM--Level II analysis using a simplified trajectory model.

> City-Specific EKMA--Level III analysis.

> Standard default EKMA conditions--Level IV analysis.

The SAI Airshed Model is a three-dimensional grid model that mathematically simulates the physical and chemical processes responsible for photochemical smog. One of the advantages offered by a three-dimensional grid model is the capability to consider spatial and temporal effects of control strategies, whereas models of less complexity consider temporal effects only. The structure of the model consists of an array of cells, and the total volume represents an urban area. The horizontal dimensions of each cell are constant, but the vertical thickness of the cells vary according to the depth of the mixed layer throughout the simulation. The

Airshed Model can simulate the advection of pollutant species through the modeling region, the diffusion of material from cell to cell, the injection of primary source emissions into the modeled region, and the chemical transformations of reactive species into intermediate and secondary products.

The SAI Airshed Model was applied to four days in 1977--21 July, 29 July, 3 August, and 2 September--to validate model predictions with station observations. Then, the model was used to evaluate control strategies under consideration for the Tulsa area. The inputs to the SAI Airshed Model serve as a data base for the series of less complex models. Descriptions of each model are presented in the following sections. Inputs to the SAI Airshed Model are summarized in the following sections and described in detail in appendix A. Inputs to the less complex models (based on the inputs from the Airshed Model) are presented in the following sections.

DEFINITION OF THE MODELS

The following list briefly describes the series of models used in this study. They are described in greater detail in the discussions that compare them. Some models are distinguished only by the mode of application.

- > The SAI Urban Airshed Model.
- > The SAI trajectory model. In terms of inputs, computations, and results at points along a selected trajectory this model differs from the Airshed Model only through the elimination of horizontal dispersion and convergent and divergent winds.
- > An EKMA-style model (OZIPM/CBM), which uses the same chemistry (Carbon-Bond) and mixing heights as the SAI trajectory model.
- > The OZIPM model (as described above) but using the regular chemistry.
- > The city-specific OZIPP model as described by the EPA (1980), but using Carbon-Bond chemistry.
- > The city-specific OZIPP model incorporating the standard EKMA chemistry as described by the EPA (1980).

In this section we wish to highlight the principal differences among the models.

Comparison of the SAI Airshed Model and the SAI Trajectory Model*

These models were designed to complement each other and, therefore, many algorithms are identical for both models (several subroutines of the computer codes are actually shared); furthermore, they use the same input files. The trajectory model begins on a square of the grid model at a specific time. The path of the trajectory is then determined solely by the wind speed and direction in the lowest level of the grid-model files. Because the other levels in the grid model often advect with velocities that are different from this lowest level, the two models often generate different results as the simulations progress in time. Nevertheless, the trajectory model provides an inexpensive method for testing parts of the grid model.

A special feature of the trajectory model is its ability to be operated backward in time. This feature was used to generate the trajectories used in this study. The time and location of either the observed or the simulated ozone maximum were used to start the backward trajectory to 0500 CDT. Thus, the forward trajectories always arrived at the desired spot at the proper time for comparison with either observations or grid-model results. Changes in emissions often lead to changes in the time and location of maximum ozone concentrations. Small changes in times of maximum ozone concentration at some specific monitoring site can be associated with rather large differences in the location of the origin of, and in the actual pathway taken by, the air parcel producing the specific ozone maximum. Therefore, when compared with a grid model, any trajectory model used as a tool for control strategies possesses the inherent shortcoming of being incapable of accounting for these changes.

Comparison of the SAI Trajectory Model and the OZIPM/CBM Model

The following similarities and differences exist between the trajectory model and the OZIPM/CBM developed for this comparison:

> Chemistry. Both models used in this study employ Carbon-Bond chemistry identical to that of the Airshed Model. However, the photolytic constants are computed differently

---

* Detailed discussions of this comparison are available elsewhere (see Reynolds et al., 1979).

in the OZIPM/CBM and SAI models. For this study, we modified the regular OZIPM/CBM values for NO_2 photolysis using a constant factor so that all models agreed at 1300 CDT. In the Airshed Model and trajectory model, the rates of all other photolytic reactions vary with NO_2 photolysis, with a fixed ratio for each; but in the OZIPM/CBM the photolysis rates vary independently. Aldehyde photolysis was adjusted in the OZIPM/CBM to give agreement between the models at 1100 CDT.

Actually, these differences in photolysis rates constitute an advantage in sophistication for the OZIPM/CBM. The NO_2 photolysis rates normally used in the OZIPM/CBM are somewhat lower than those used in the SAI models, which are based on actual measurements. Since the purpose of the present study was to compare the OZIPM/CBM with computed results of the Airshed Model, we were forced to alter the OZIPM/CBM models to eliminate this difference.

The use of fixed ratios to NO_2 photolysis in the SAI models in place of the variable ratios used in the OZIPM/CBM model may lead to some minor differences in chemistry. The ratios are at a maximum at solar noon and a minimum at sunrise and sunset (Whitten, Killus, and Hogo, 1980). The photolysis rates for aldehydes change more with solar zenith angle than the NO_2 photolysis rate does because aldehydes photolyze at the short wavelength end of the solar spectrum, whereas NO_2 photolyzes nearer the long wavelength end of the ultraviolet spectrum. The short ultraviolet wavelengths are more affected by the ozone in the stratosphere than are the longer wavelengths. At high zenith angles (morning and evening), the solar rays must pass through a thicker layer of ozone. Therefore, the ratio of aldehyde photolysis to NO_2 photolysis varies throughout the day, reaching a maximum at solar noon. For this particular study, the OZIPM/CBM aldehyde photolysis values were multiplied by a constant value throughout each day so that the models agreed at 1100 CDT. Therefore, in the early morning the photolysis rate of the aldehydes in the OZIPM/CBM would be somewhat less than that used in the SAI models.

For this particular study, we chose to modify the OZIPM/CBM to make it as much like the Airshed Model and trajectory model as possible. By removing all possible potential variables between models, we hoped to be able to better compare the fundamentals underlying these models. The CBM version of OZIPM/CBM has normally been applied to assist users of the Airshed Model to estimate potential control scenarios. For such applications the photolysis adjustments discussed here are normal.

> Reactivity. The SAI trajectory model and Airshed Model are operated with reactivity splits that vary with each source category. However, the OZIPM/CBM does not have this feature; instead, reactivity is assumed to be constant for all hydrocarbon emissions throughout the day. For this study, the OZIPM computer code was modified so that three different hydrocarbon reactivities could be used: one for the initial conditions, one for the aged hydrocarbons aloft, and one for the emissions that occur throughout the day. Hence, the only differences in reactivity were in the temporal variations aloft and in the variable emissions used in the SAI models compared with the fixed reactivities employed in the emissions for the OZIPM models. The reactivities used in the OZIPM/CBM were determined from averages of emissions used in the trajectory model; for averaging the hydrocarbons aloft, a weighting factor was used each hour that was equal to the positive change in mixing height.

In a sense, the NO_2/NO_x ratio also acts as a reactivity effect. The OZIPM/CBM uses a fixed ratio of NO_2/NO_x (10 percent) for all NO_x emissions, whereas the SAI models allow this ratio to vary according to their source category (the average ratio is typically about 5 percent). At this time, we have not attempted either to change the OZIPM/CBM or to fix the ratio in the SAI model, because we feel the difference is trivial. For NO_x aloft, the OZIPM/CBM uses pure NO_2, which is close to typical values found in the trajectory model simulations because the NO_2/NO_x ratio is almost always greater than 0.85; often, the values are greater than 0.99.

> Integration Scheme. The OZIPM/CBM uses a Gear-type method without any steady-state approximations, whereas the trajectory model uses the same Crank-Nicholson finite differencing scheme and steady-state approximations that are used in the Airshed Model. Again, this difference in model sophistication is opposite from the direction

intended by our series of models. However, our previous tests using smog chamber experiments suggest that the differences introduced by the numerical integration schemes should be minimal.

> Vertical Layers. The Airshed Model and trajectory model share the same vertical layers and algorithms for numerical integration, but additional contributions are introduced into the Airshed Model for convergent or divergent winds. The OZIPM/CBM, of course, is limited to providing calculations of the mixed layer as a whole, but fixed concentrations in the layer aloft can be introduced as the mixing height rises. The SAI models account for mixing within the mixed layer, mixing within the inversion layer, and eddy diffusion among all layers. The OZIPM/CBM assumes instantaneous mixing within the entire mixed layer, and no eddy diffusion is considered across the boundary defined by the mixing height.

In our comparison studies, the effectiveness of multilayers and eddy diffusion was one of the central issues to be evaluated in this region of our model series. A problem that we tried to avoid, which does confound the comparison, is the entrainment of pollutants from aloft. The OZIPM/CBM requires fixed concentrations aloft, so these must be chosen from some "proper" average of the time-dependent concentrations computed in the SAI trajectory model. With the average value used in this study we attempted to weight most heavily the concentrations entrained when the mixing height rises most significantly. A more complex weighting scheme might involve the time when the greatest effect on the chemistry occurs; however, this effect was not evaluated. Concentrations aloft are not considered for the time before the inversion rises or after it has reached some maximum. As the mixing lid drops late in the afternoon, the only process affecting the surface layer from concentrations aloft is eddy diffusion. Eddy diffusion is treated in the Airshed Model and trajectory model, but is neglected in the OZIPM/CBM.

> Mixing height. All models used in the OZIPM/CBM that are based on the OZIPM computer code, as well as the Airshed Model and trajectory model, can use identical mixing heights with values that vary linearly in time between specified values at each hour.

- Temperature. The temperature varies in the Airshed Model and trajectory model, but the OZIPM/CBM currently employs a fixed temperature. This difference can be significant. Temperature affects both vertical diffusion and chemistry in the SAI models, but it can affect only chemistry in the OZIPM/CBM because vertical mixing is assumed to occur instantaneously within the mixed layer.

- Emissions. The Airshed Model and trajectory model allow for emissions into all layers; the OZIPM/CBM treats all emissions in the mixing layer alike and does not directly address emissions above the mixing layer. For the layer aloft in the OZIPM/CBM, the emissions must be accounted for in the determination of the fixed concentrations aloft. The sum of the emissions used in the lower layers of the trajectory model was used for the mixing layer in the OZIPM/CBM. For this study, the OZIPM computer code was modified to treat emissions in an absolute fashion rather than as a multiple of the initial conditions. This was implemented by using the transported surface layer inputs as the initial concentrations. The normal initial concentrations (the CALC mode in OZIPM) were specified as 1.0 for both HC and NO_x, but these values were not added as initial concentrations. They were used only for emission fraction development because emissions are expressed relative to these values in the OZIPM code.

- Emissions for the SAI models are given as total moles emitted into each cell during each hour. To arrive at values appropriate for the OZIPM/CBM we used the following conversion procedure: the mixing volumes of the trajectory model and the OZIPM/CBM were assumed to be equal below the mixing height, such that

  $$V = A \times Z_{mix} \quad ,$$

  where A is the area of the horizontal cross-section of the air parcel defined in trajectory model simulations, and Z_{mix} is the mixing height. If the volume is expressed in cubic centimeters, the moles emitted in one hour (the number available from the trajectory model computer output) can be divided by this volume to give moles/cm^{-3} units. This, in turn, can readily be converted to the OZIPM/CBM units of concentration, ppm, by using a conversion factor of 2.445×10^{10} ppm $moles^{-1}$ cm^3, which is technically correct for a perfect gas at 298 K and 1 atmosphere of pressure. The numbers calculated at this point are almost directly applicable to the OZIPM/CBM model. First, the use of 1.0 for the initial concentrations of HC and NO_x in the CALC mode implies that each one-hour emissions number would be the concentration added during the hour if the mixing height were the same as the initial value Z_0. However, the computer codes are written so that, at each instant in time, the emissions factor is multiplied by Z_0/Z_{mix}. Therefore, the Z_{mix} drops out and the actual numbers (E_n) used are merely

$$En = A \times 2.445 \times 10^{10}/Z_0 \quad ,$$

where A and Z_0 are expressed in centimeters.

In this particular study, it was occasionally necessary to use special emissions factors. These factors were used for those cases in which the trajectory model employed substantial initial conditions for the first two layers (up to 100 m) even though the mixing height was only 50 m. Since there was typically an order-of-magnitude difference in concentration between the initial conditions below 100 m and the layers above this level, there was no way to compute a reasonable average value to be used in the OZIPM/CBM for the layer aloft. Therefore, the initial conditions between 50 and 100 m used in the SAI models were treated as emissions in the OZIPM/CBM. These "emissions" were added to the normal emissions during the hour when the mixed layer in the SAI models jumped from 50 to 100 m. For these cases the appropriate OZIPM/CBM emissions factors merely add to the normal emissions, since the initial mixing height is 50 m and the height added is also 50 m.

Comparison of the OZIPM/CBM Model and the (OZIPM) Model

The OZIPM/CBM and the OZIPM models differ only in the photochemical mechanism each employs. The OZIPM model uses the propylene/butane chemistry as described by Dodge (1978). The obvious intention of this comparison was to evaluate only the differences between the Carbon-Bond chemistry and the standard propylene/butane chemistry. Although the OZIPM computer program was specifically written to handle such comparisons, some complications were introduced when the OZIPP was operated with the propylene/butane chemistry. The Carbon-Bond chemistry used in this study assumes that formaldehyde and ketones represent half of the total aldehydes found in the simulation, whereas the formaldehyde in the OZIPM is only 40 percent of the total amount of aldehydes. The photolysis rates used in the Airshed Model runs are based on a theoretical solar radiation function that does not contain the updated NO_2 absorption cross sections. The OZIPM simulations use the latest NO_2 cross sections, which are approximately 10 percent lower than those used in the Airshed Model.

The reactivity of the two mechanisms was not typically adjusted in this study. The total HC concentrations and emissions rates were identical for these two models, but the propylene/butane chemistry was typically used with the standard 25 percent propylene, 75 percent butane, and 5 percent aldehyde reactivity.

Comparison of the OZIPM Models and the City-Specific EKMA (OZIPP) Model

The basic assumptions for the inputs to the OZIPM and OZIPP models are essentially the same (i.e., taken from the Airshed Model data base), but the method of defining inputs differs between the two models. Whereas the OZIPM models consider initial conditions at 0500 CDT, the OZIPP (city-specific EKMA) model simulations begin at 0800 CDT.

Another difference between the OZIPM and the city-specific EKMA is the use of variable mixing-height inputs in the former, more sophisticated, version. In the OZIPM, instantaneous mixing heights are computed by linear interpolations between hourly input values rather than by the OZIPP method, which uses an exponential interpolation between the morning and afternoon mixing heights. The exponential increase in mixing height with time provides a constant dilution factor. In addition to the potential problems associated with the assumed shape of the mixing-height time profile, the standard OZIPP cannot consider a decrease in mixing height that may follow an increase, nor can it consider a resumption in mixing-height growth following a decrease or a pause.

The OZIPM is based on trajectory paths that contain emissions of NMHC and NO_x specific to each path. The city-specific EKMA, on the other hand, uses county-wide emissions estimates, which vary only between counties.

Inputs developed for the city-specific EKMA are based directly on monitoring station observations, whereas the OZIPM model inputs are based on the inputs of the Airshed Model. Although the Airshed Model inputs are also based on monitoring data, the inputs are in some cases "tuned" within the uncertainties of the measurement to give closer ozone agreements between predictions and observations.

DESCRIPTION OF THE TULSA MODELING REGION

The Tulsa area consists of an isolated metropolitan area (Tulsa, Oklahoma) surrounded by smaller cities. Unlike the Los Angeles region and numerous cities located in the northeastern United States, the Tulsa region clearly defines the locations of the principal sources of emissions and precursor transport. A map of the Tulsa area is shown in figure 3-1.

CHARACTERIZATION OF THE TULSA MODELING DAYS

From the extensive monitoring study reported by Eaton et al. (1979a, 1979b; Eaton and Dimmock, 1979) during the summer of 1977, four days were chosen for the validation of the SAI Airshed Model. The maximum observed ozone concentration for the four days is presented in table 3-1. We note that throughout this section any reference to time represents time at the beginning of the hour (e.g., 0500 CDT represents 0500-0600 CDT).

This section describes the meteorological and air quality conditions associated with the 21 July, 29 July, 3 August, and 2 September 1977 study days, considering, in particular, the general transport characteristics of each day and the resulting pollutant patterns observed over the monitoring network. Much of the following discussion was taken from Reid, Reynolds, and Oliver (1980) and reflects different meteorological air quality conditions of interest for SAI Airshed Model validation. As discussed in the following sections, the same conditions for these validation days were used throughout the series of models. We note that Eaton et al. (1979c) have carried out an extensive examination of several interesting days for the 1977 field study in Tulsa that includes the four days of interest here. We have found their analyses to be quite helpful in preparing this description.

Characterization of 21 July 1977

The 21 July 1977 study period was chosen because the meteorological conditions recorded for a large portion of this day were representative of those most frequently observed in Tulsa during the summer of 1977. A weak high-pressure area situated over northern Florida produced southerly winds in Tulsa throughout the morning and early afternoon. This flow pattern was consistent with the 0700 CDT rawinsonde data collected at Oklahoma City, which indicated that winds averaged over the lowest 1000 meters were out of the southwest. Temperature data obtained from this sounding also suggest the presence of stable air throughout the lowest 4000 meters of the atmosphere.

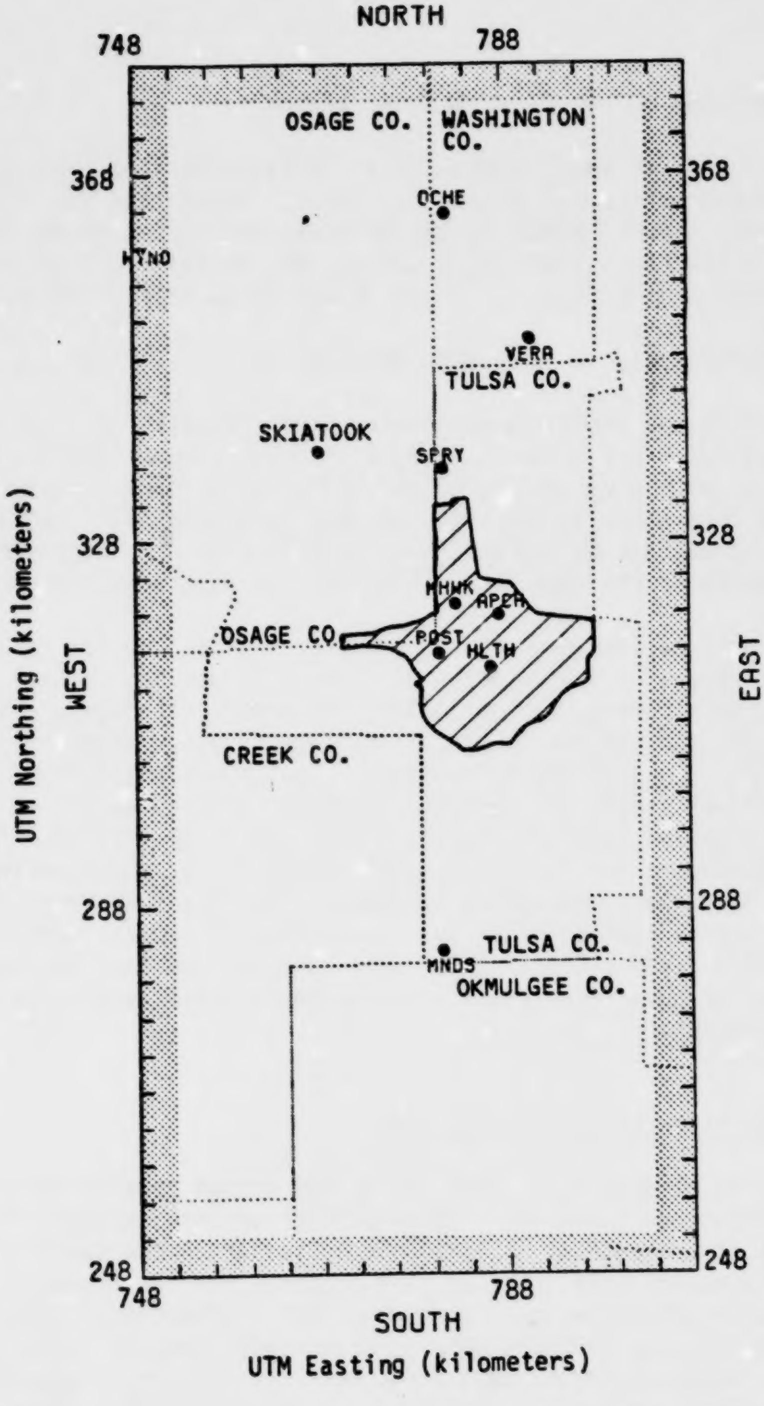

NORTH
748
788
OSAGE CO.
WASHINGTON CO.
368
OCHE
WYNO
VERA
TULSA CO.
SKIATOOK
SPRY
328
MHWK
APCH
OSAGE CO.
POST
HLTH
CREEK CO.
288
MNDS
TULSA CO.
OKMULGEE CO.
248
WEST
EAST
SOUTH
UTM Northing (kilometers)
UTM Easting (kilometers)

Figure 3-1. The gridded Tulsa modeling region.

TABLE 3-1. MAXIMUM OBSERVED OZONE CONCENTRATION FOR THE FOUR MODELING DAYS IN 1977

(ppm)

Date	Location of Maximum Concentration	Time of Occurrence of Maximum Concentration (CDT)	Maximum Observed Concentration
21 July	Vera	1300	0.14
29 July	Apache	1400	0.17
3 August	Vera	1500	0.15
2 September	Ochelata	1500	0.11

The NWS surface weather map for 0700 CDT indicated a cold front located in the panhandle regions of Oklahoma and Texas. By midafternoon, reduced solar radiation caused by increased cloudiness marked the arrival of the front in the Tulsa area. At this time the prevailing southerly winds gave way to a more stagnation-like condition that comprised light westerly and northerly winds at the surface. However, the average wind direction observed over the lowest 1000 meters in Oklahoma City at 1900 CDT was from the southeast.

Precursors emitted during the morning were carried to the north, resulting in a maximum hourly averaged O_3 level of 0.135 ppm that was observed at Vera. The ozone concentrations at Sperry and Ochelata were higher than those reported at Skiatook and Wynona, which suggests that pollutants from Tulsa were transported to the north or northeast and not to the northwest. With the onset of cloudiness in the midafternoon, observed ozone levels decreased at all stations in the network.

Characterization of 29 July 1977

This day is of particular interest because ozone concentrations measured at the Apache station exceeded 0.16 ppm during four consecutive hours in the middle of the day. In addition, the maximum value of 0.166 ppm at this station was the highest value reported for the entire 1977 summer study period. Another interesting facet of this day is the fact that the ozone values observed at the three other city stations (post office, health department, and Mohawk) generally did not exceed 0.12 ppm. Although the greatest distance between any two city stations was less than 8 kilometers, substantial spatial gradients in the ozone field were observed.

On 28 July, a large high-pressure area was centered over the northeastern portion of the country, and a stationary front was situated just south of the Oklahoma and Texas borders. The Tulsa area experienced overcast skies throughout the day, yielding lower-than-average temperatures. In general, the winds were relatively light and out of the south.

By the morning of 29 July, the stationary front was positioned just north of Tulsa, and during the predawn hours ozone concentrations at several stations exhibited an increase. Eaton et al. (1979a) attributed this unexpected occurrence to a disturbance caused by a frontal passage that enabled ozone aloft to reach the ground. Ozone levels during this time typically rose to about 0.04 ppm.

The 0700 CDT rawinsonde data taken at Oklahoma City indicated that the winds in the lowest 1000 meters of the atmosphere were from the north, whereas the winds in between 2000 and 3800 meters of the atmosphere were out of the south. The early-morning surface winds in the Tulsa area were from the southwest. At about 1100 CDT, the surface winds at Wynona and Ochelata exhibited a shift to a north-northeasterly orientation. The southwesterly and northeasterly winds in the southwest and northeast portion of the modeling region, respectively, seemed to combine to produce light, southwesterly winds in the Tulsa city area throughout the mid-morning to early-afternoon period.

By 1400 CDT, the winds at Liberty Mounds exhibited a northerly orientation that seemed to indicate a transition to northerly winds throughout the network. In the afternoon, the urban plume was transported to the south, which is illustrated by the fact that the ozone concentrations at Liberty Mounds suddenly increased from a steady, early-afternoon value of about 0.08 ppm to a value of 0.12 ppm at 1700 CDT. In the late afternoon, the surface winds exhibited yet another shift, this time to a southerly orientation. Ozone at Liberty Mounds then decreased to a level more characteristic of ozone levels observed at that station earlier in the day. At the same time, the ozone levels observed at the post office site (to the north of Liberty Mounds) showed an increase. A peak hourly concentration of 0.11 ppm was measured at 1900 CDT.

Characterization of 3 August 1977

This day is of interest because of the observation of relatively high ozone concentrations at stations to the north of Tulsa. In fact, the second highest hourly averaged ozone concentrations for the summer field study conducted at Sperry, Vera, and Ochelata--0.135, 0.151, and 0.114 ppm, respectively--were reported on this day.

On 3 August, a stationary front was located near the Gulf Coast, and a ridge of high pressure was situated to the east of Oklahoma. It is likely that the front was responsible for the stalling of synoptic systems that led to stagnation conditions in the Tulsa area. During the morning, the skies were overcast and did not clear until about 1100 CDT. The reduced solar radiation led not only to lower morning mixing heights, but also to the delay of photochemical reaction phenomena until the late-morning period.

The 0700 and 1900 CDT rawinsonde data recorded at Oklahoma City indicated that the winds aloft were out of the south over the lowest 2500 meters of the atmosphere. Southerly winds were also observed at the surface in Tulsa during the early-morning hours at all sites except Liberty Mounds, which reported easterly winds. (We note that the winds measured at Liberty Mounds throughout a significant portion of this day were inconsistent with those reported at the other stations.) Between 0800 and 1400 CDT, the winds at each station (except Liberty Mounds) were observed to undergo a systematic clockwise rotation. For example, the hourly averaged directions reported at the health department site for the hours 0800 to 1400 CDT were 189, 234, 288, 360, 45, 135, and 171 degrees, respectively. By 1400 CDT, southerly winds were again reestablished in the Tulsa area.

Because of the wind conditions cited above, early-morning precursors were initially transported to the north and east. As the morning progressed, transport to the south and west probably brought an already polluted air mass back into the vicinity of the city. With the onset of southerly winds at midday, it is possible that additional emissions were injected into the air parcel as it crossed the city and was transported to the north. Ozone concentrations at Liberty Mounds exhibited a continuous increase throughout the morning and peaked at 0.103 ppm between 1300 and 1400 CDT. It is likely that some of this ozone may have resulted from the reaction of precursors that were emitted earlier in Tulsa and that were subject to southern transport during a portion of the morning. Late-morning ozone concentrations at other rural stations were somewhat lower.

Characterization of 2 September 1977

This day was selected for evaluating SAI Airshed Model performance to include at least one period during which the supplemental upper-air observation program was in effect. The primary influence on the meteorology in Tulsa for this day was a high-pressure area centered over the mountainous regions of North Carolina, Virginia, and West Virginia. The winds were generally out of the south throughout the day, and the skies were mostly clear. During the early-morning hours, the surface winds were relatively light, indicating that little pollutant transport was occurring. However, after 1200 CDT, surface winds in excess of 10 mph were observed.

Three sets of integrated hydrocarbon grab samples were collected at the Liberty Mounds, health department, post office, and Sperry sites during the day. These were three-hour samples taken from 0600 to 0900, 0900 to 1200, and 1400 to 1700 CDT. During the 0600 to 0900 CDT sampling period, the hydrocarbon composition at the two city sites was largely representative of motor vehicle exhaust. At Sperry, however, a high percentage of low-molecular-weight hydrocarbons was reported, indicating that earlier emissions from the oil refining and storage facilities to the south had been carried by the southerly winds to the Sperry area. The 0900 to 1200 CDT sample collected at the post office site also contained a large fraction of low-molecular-weight hydrocarbons. Since the winds at this time were southerly to southwesterly, it is likely that these measurements are also reflective of emissions from the petrochemical complex. Hydrocarbon concentrations recorded in the 1400 to 1700 CDT bag samples were relatively low, suggesting the effect of increased mixing and removal by photochemical reaction.

Air quality measurements taken aloft using an instrumented aircraft were obtained during both the early morning and the early afternoon. Each flight consisted of a combination of vertical spirals and horizontal traverses oriented upwind (to the south) and downwind (to the north) of the city during the morning and afternoon periods, respectively. Although the early morning NO and NO_2 concentrations aloft were found to be very low, a background ozone level of about 0.06 ppm was observed. The afternoon flight took place between 1302 and 1535 CDT, and a clear, urban ozone plume was observed during the east-west horizontal traverses at 2500 feet MSL to the north of the city. A maximum ozone concentration of 0.156 ppm was measured on a horizontal traverse that passed just to the south of Ochelata.

The measured ground-level ozone concentrations to the north of Tulsa in the afternoon also indicate the presence of an urban plume. The plume began to form at about 1100 CDT and was transported to the north. Ozone concentrations at Ochelata were relatively constant during the time from 1000 to 1400 CDT, ranging between 0.053 to 0.060 ppm. During the next two hours, the measured ozone levels increased, signifying the arrival of the plume in the Ochelata area. The highest hourly averaged ground-level ozone concentration of 0.108 ppm on this day was observed at Ochelata between 1500 and 1600 CDT. At 1500 CDT, the winds shifted from a southerly to a southeasterly direction; the ozone values at Ochelata began to decrease, and concentrations at stations to the west increased. The maximum ozone concentrations at Skiatook and Wynona were reported at 1600 and 1800 CDT, respectively.

INPUTS USED IN THE SAI AIRSHED MODEL SIMULATIONS

Detailed descriptions of the methodologies used in describing the meteorological, emissions, and boundary concentration inputs used in the SAI Airshed Model are presented in appendix A of this document. In this section, we summarize some of the inputs used for each of the four modeling days.

The study region used in the SAI Airshed Model simulations was defined during the development of the emission inventory by Engineering Science (1979). The modeling region itself is 52 km by 124 km consisting of 403 square grid cells. Each grid cell is 4000 meters in length.

Surrounding each side of the modeling region is a row of cells representing the boundary cells and containing the boundary conditions (concentrations) used in the SAI airshed simulations. A map of the modeling region is shown in figure 3-1, presented earlier.

Initial conditions for ozone, NO_x, and hydrocarbons in the surface layer were defined on the basis of monitoring station observations for each of the modeling days. The surface initial conditions are shown graphically for NO_x and hydrocarbons in figures 3-2 and 3-3 for 21 July and 3 August. A spatially uniform NMHC value of 0.2 ppmC was used for the 29 July modeling day.

Boundary conditions for the four modeling days are shown in table 3-2. These boundary conditions were used for the cells along the horizontal edges and in the aloft layers of the modeling region.

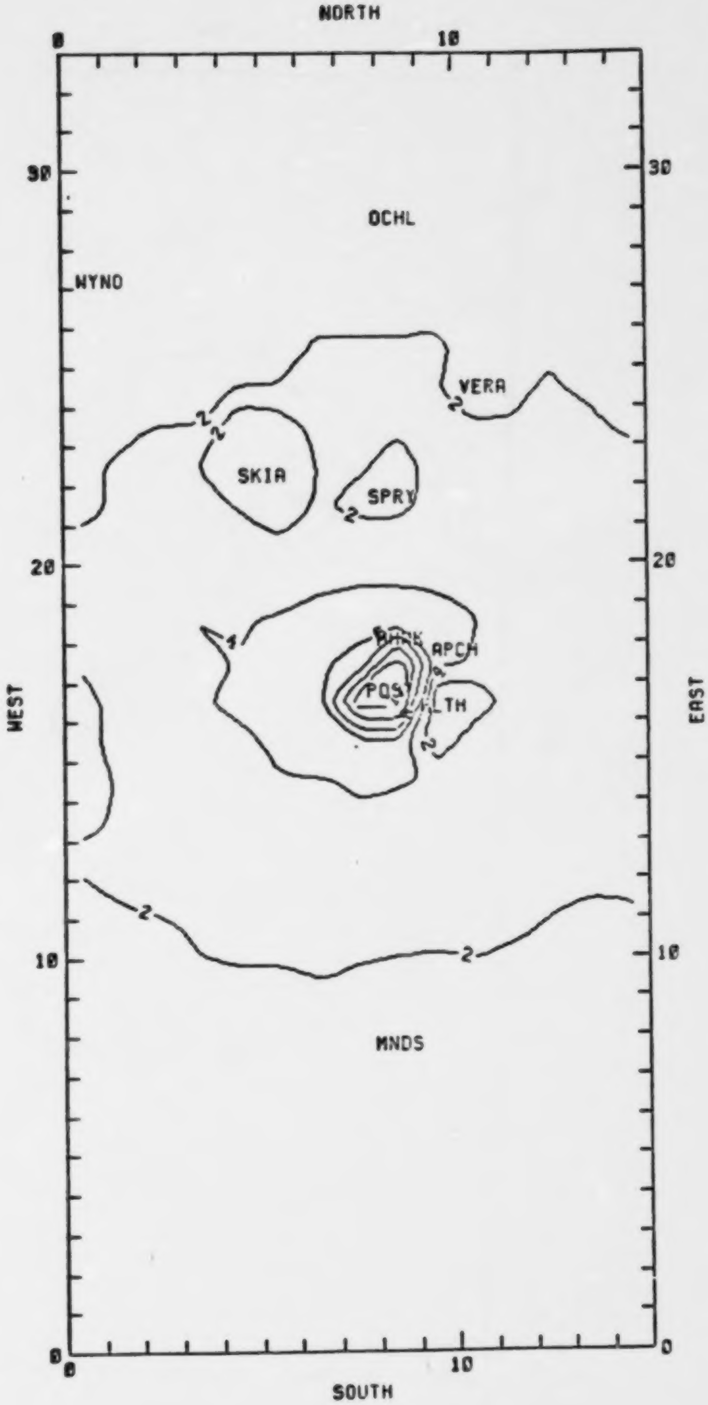
Mixing height profiles were developed for each day using temperature soundings taken at the Tulsa airport. Mixing heights were spatially constant over the rural and urban regions during most of the day. Mixing heights over the urban region were set higher in the morning and late afternoon hours for 21 July, 29 July, and 2 September. Mixing height profiles are shown graphically in figure 3-4 for the four modeling days.

Three-dimensional wind fields were generated from station measurements for each of the modeling days. Wind fields for selected hours are shown in appendix A (figure A-3). In general, winds are usually from the south and southwest during the morning hours. Southerly winds may persist throughout the day. On certain days the winds are from the north and east during the afternoon hours, which leads to a turning of the air parcel around the urban area. This effect occurred on 29 July and 3 August. Air parcel trajectories derived from the SAI trajectory model (discussed in the following sections) show the turning effect around the urban area.

Emissions inventories for the Tulsa area were developed by Engineering-Science (1979). The emissions inventory reflects both ground-level and elevated point sources of hydrocarbon and NO_x. Emissions totals are summarized in section 5 of this document (table 5-1). Spatial distributions of each of the Carbon-Bond species in the emissions inventory are shown in table A-6 of appendix A.

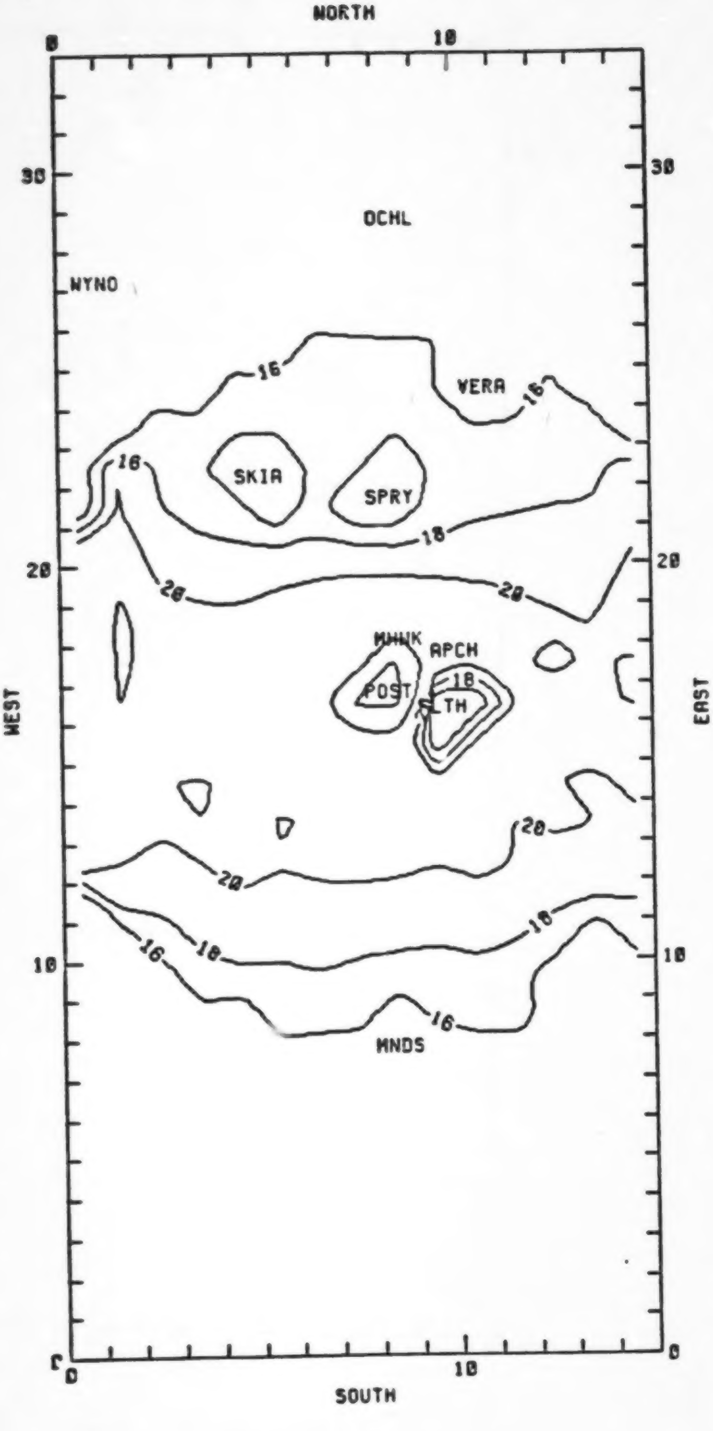
INPUTS USED IN THE SAI TRAJECTORY MODEL SIMULATIONS

The meteorological and emissions files used in the SAI trajectory model are the same as those used by the SAI Airshed Model. By running the SAI trajectory model in the backwards mode, we can determine a path to the


NORTH
0
10
30
30
OCHL
WYNO
VERA
2
2
2
SKIA
SPRY
2
20
20
1
APCH
POS
LTH
2
WEST
EAST
2
2
10
10
MNDS
0
0
0
10
SOUTH

(a) For NO_x (ppb)

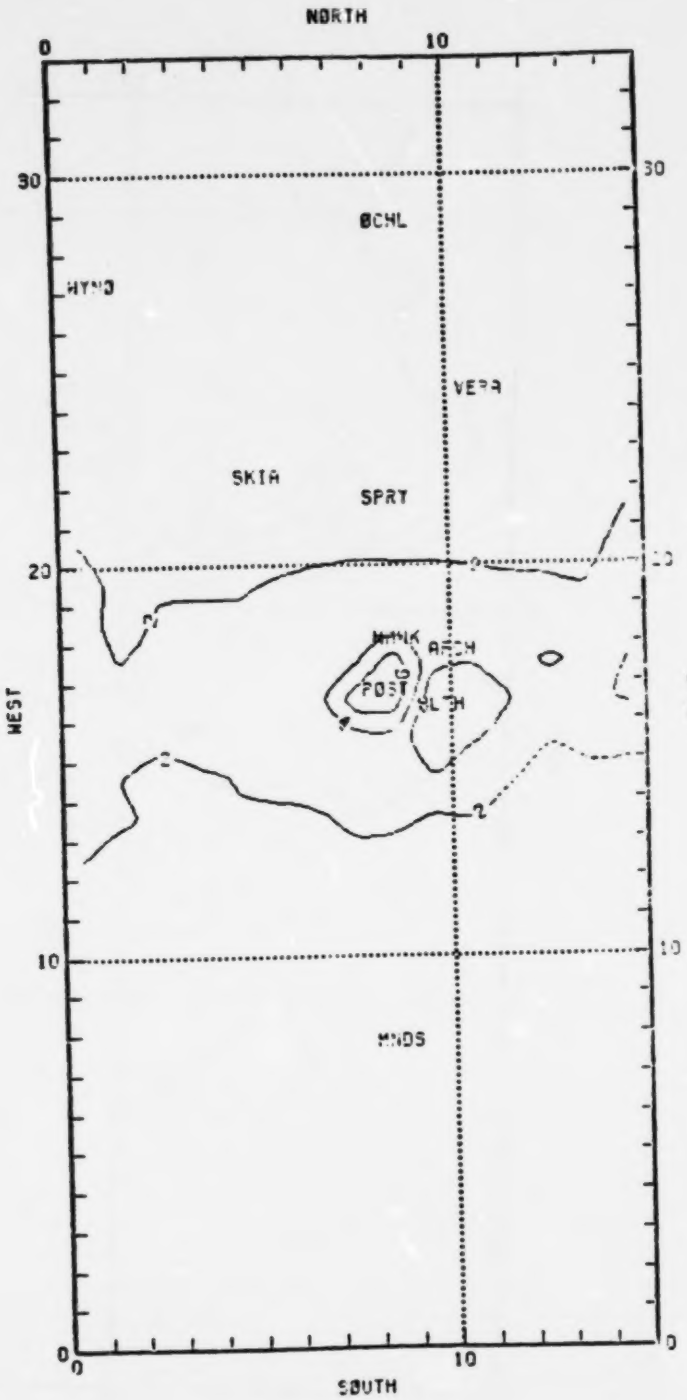
Figure 3-2. Initial conditions in the ground-level grid cells on 3 August 1977 (isopleths in increments of 2 pphm).


NORTH
0
10
30
30
OCHL
WYNO
16
VERA
16
16
SKIA
SPRY
18
20
20
20
WEST
WHWK
APCH
POST
18
LTH
EAST
20
20
18
16
18
10
10
16
MNDS
0
0
10
SOUTH

(b) For RHC (pphm)

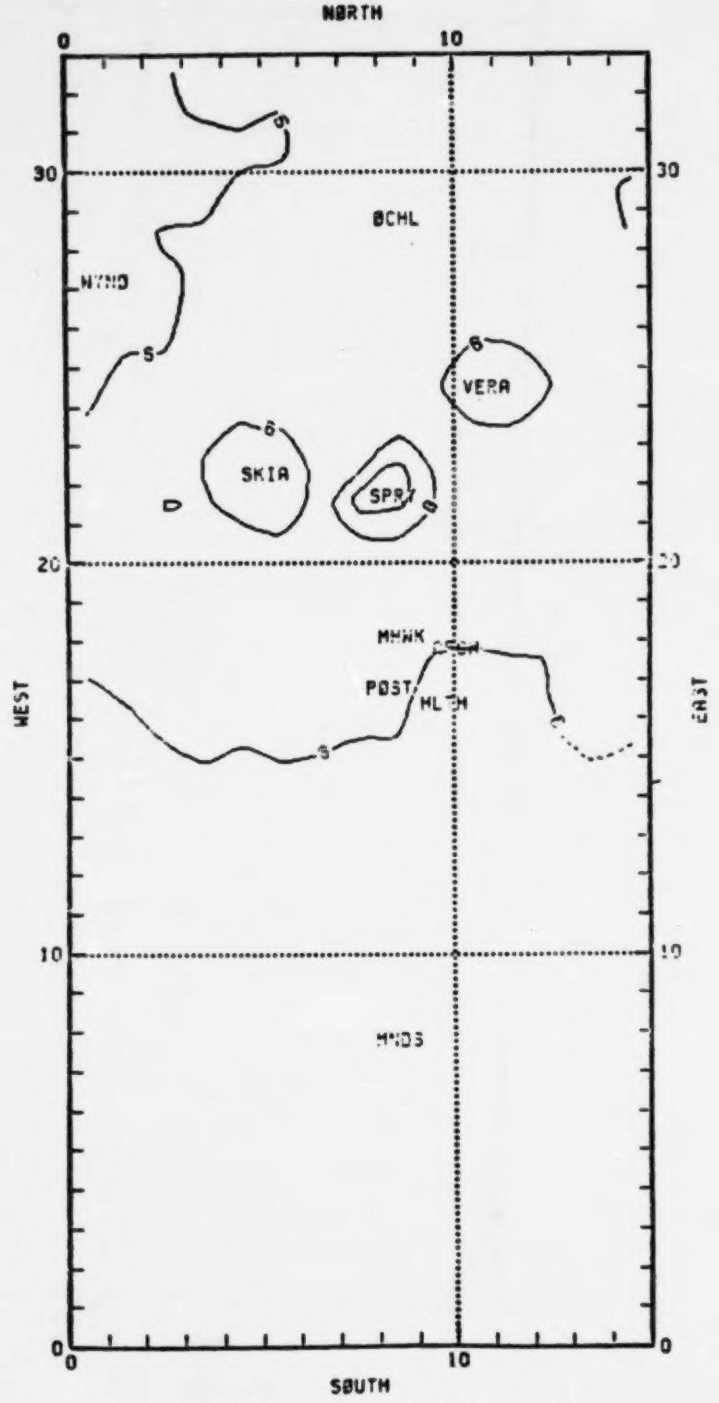
Figure 3-2 (concluded).

49r 81 18


NORTH
0
10
30
BCHL
HYND
VERA
SKIA
SPRT
20
2
MANK
ARCH
6
POST
BLTH
4
WEST
EAST
2
10
MNDS
0
0
10
0
SOUTH

(a) For NO_x (ppb)

Figure 3-3. Initial conditions in the ground-level grid cells on 21 July 1977.


NORTH
SOUTH
WEST
EAST
0
10
20
30
BCHL
NYND
VERA
SKIA
SPRV
MHWK
POST
HLTH
MNDS
5
6

(b) For RHC (pphm)

Figure 3-3 (Concluded).

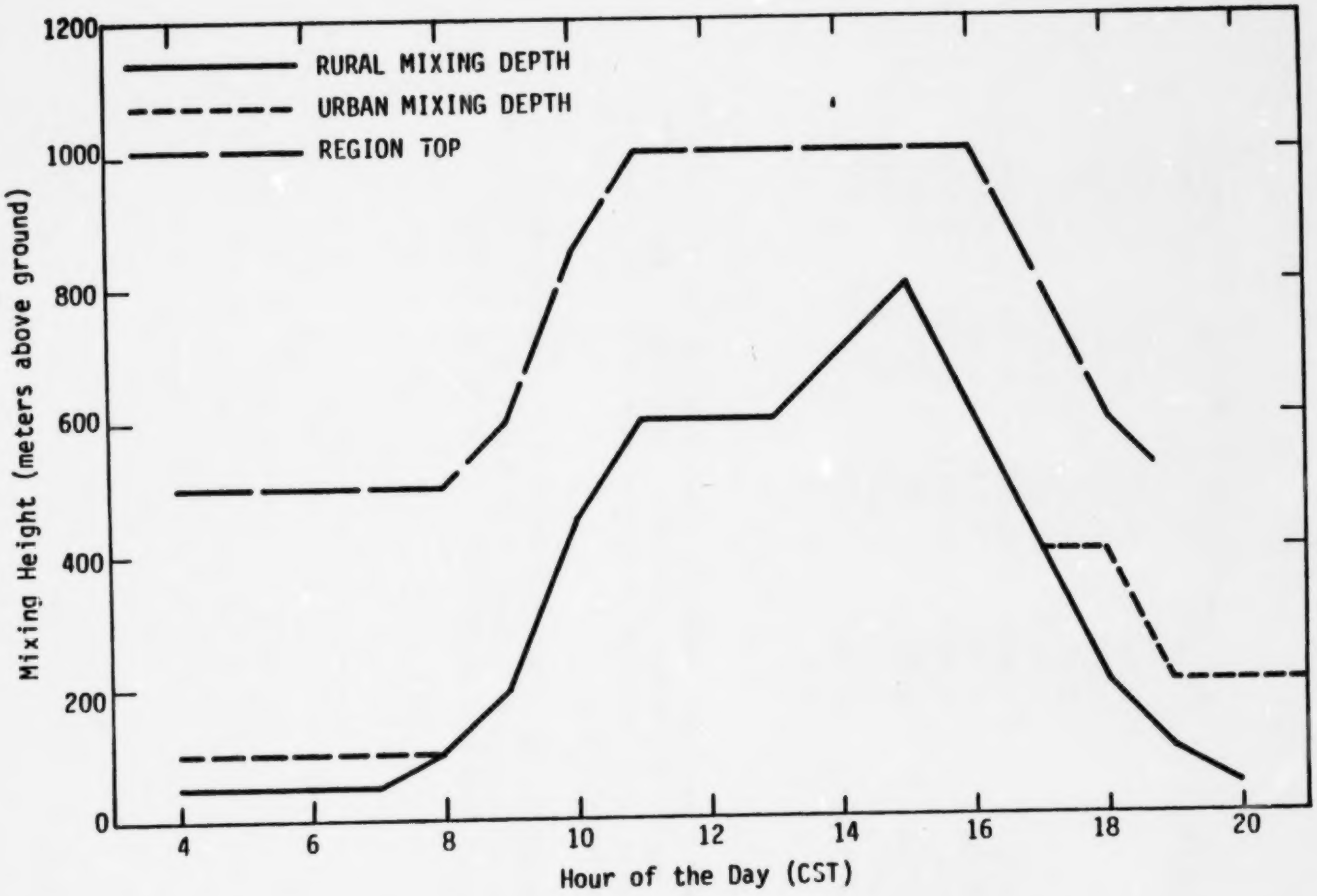
TABLE 3-2. BOUNDARY CONCENTRATIONS USED IN THE TULSA SIMULATIONS (ppm)

Species	Boundary Concentrations 21 July	 29 July	 3 Aug.	 2 Sept.
NO	0.0001	0.0005	0.0005	0.0005
NO_2	0.002	0.002	0.002	0.002
O_3	0.06	0.08*	0.06	0.05†
NMHC	0.24	0.20	0.21	0.17
Ethylene	0.0058	0.0049	0.0051	0.0041
Paraffins	0.065	0.053	0.056	0.046
Olefins	0.0014	0.0012	0.0013	0.0010
Aromatics	0.012	0.009	0.010	0.008
Carbonyls	0.012	0.009	0.010	0.008
Benzaldehyde	0.00001	0.00001	0.00001	0.00001
CO	0.1	0.1	0.1	0.1

---

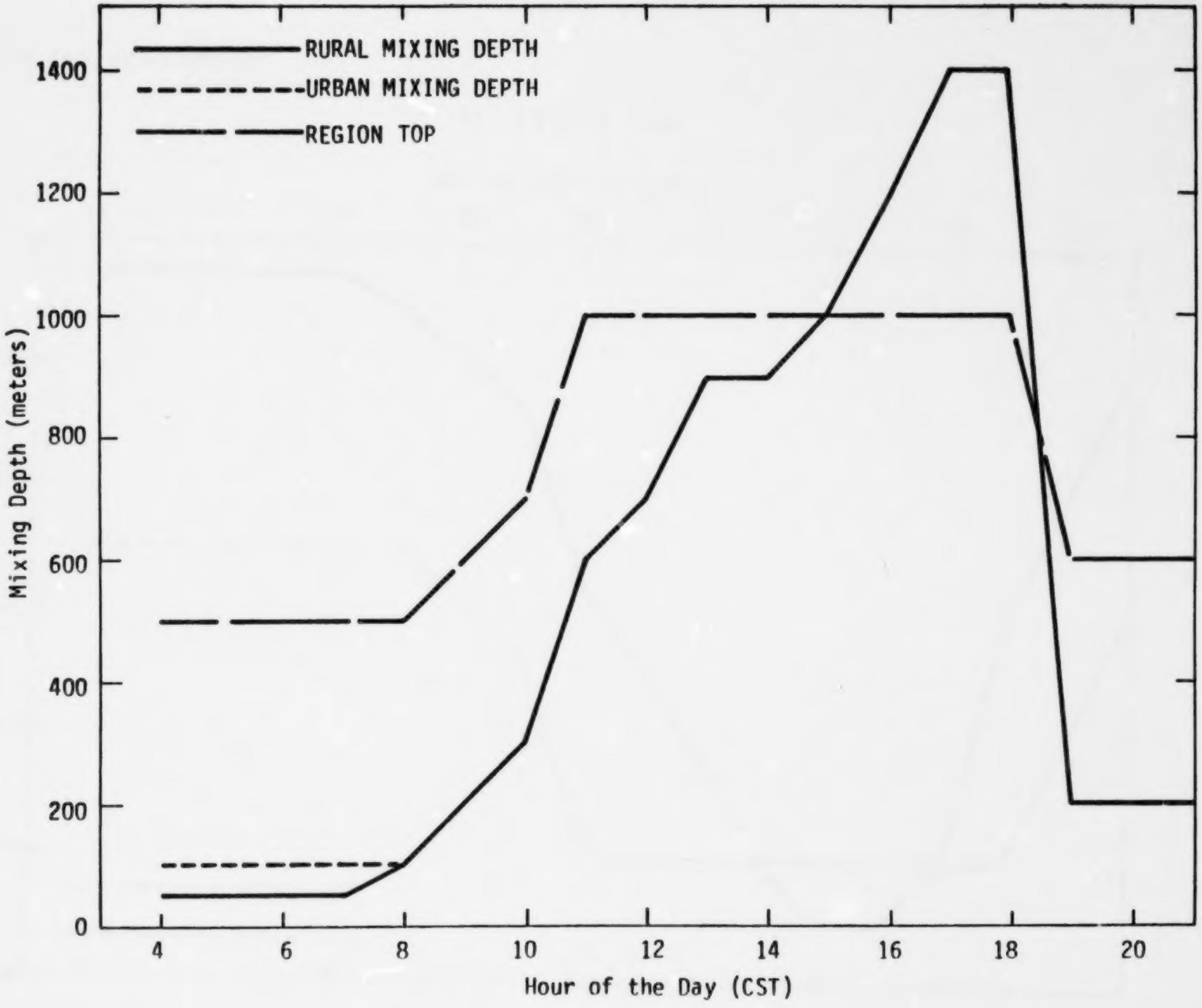
* For 29 July, the ozone boundary concentrations on the sides of the modeling region varied with location. The boundary values on the north, south, east, and west boundaries were 0.07, 0.08, 0.06, and 0.08 ppm, respectively.

† For 2 September, the O_3 boundary concentration at the top of the modeling region varied in time: From 400 to 1100 CST, it was set at 0.07 ppm and from 1100 to 2100 CST, it was set at 0.05 ppm.



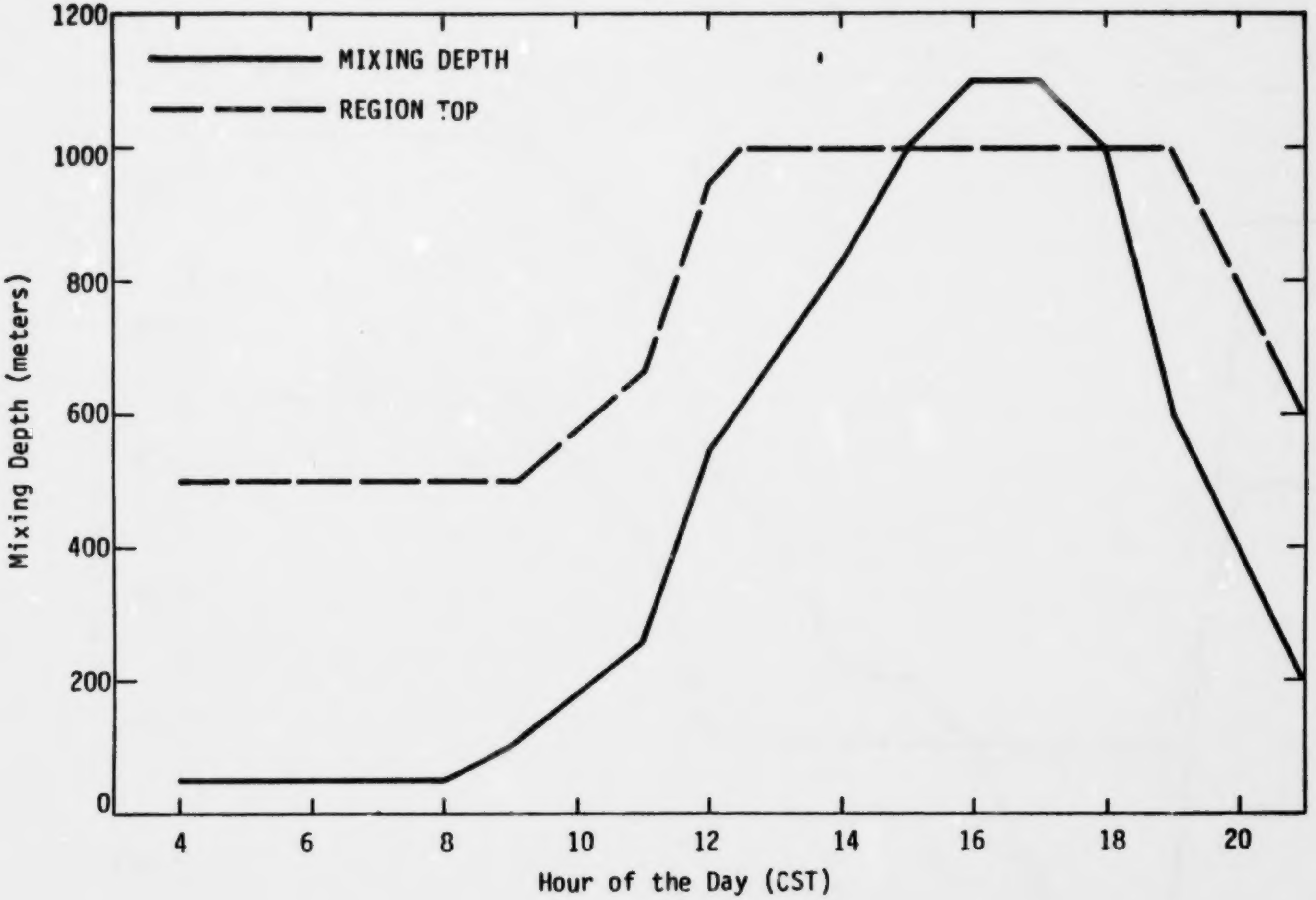
(a) For 21 July 1977

Figure 3-4. The diurnal pattern of the mixing depth and top of the modeling region



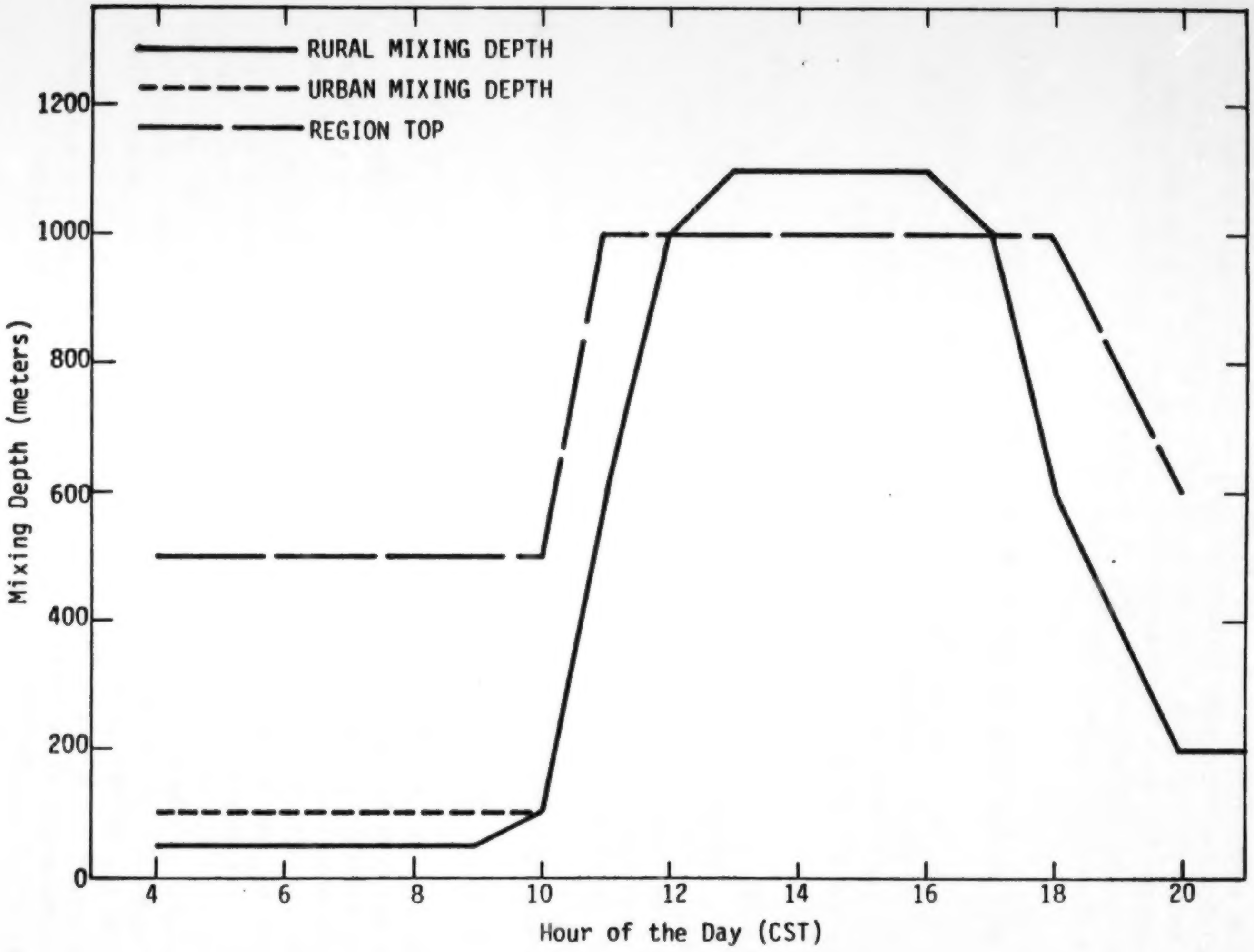
(b) For 29 July 1977

Figure 3-4 (Continued).



(c) 3 August 1977

Figure 3-4 (Continued).



(d) For 2 September 1977

Figure 3-4 (Concluded).

maximum ozone observed for the day of interest. This path is based on the wind fields in the first vertical layer only. As discussed earlier the use of the wind fields in only the first layer can lead to differences in the predicted maximum ozone between the SAI trajectory model and the SAI Airshed Model on days with wind shear. From the locations of the maximum ozone observed for each day presented earlier in table 3-1, we determine the path to the maximum ozone. The trajectory paths for the four modeling days are shown in figures 3-5(a) through 3-5(d).

INPUTS USED IN THE LEVEL II CBM/OZIPM AND LEVEL II OZIPM MODEL SIMULATIONS

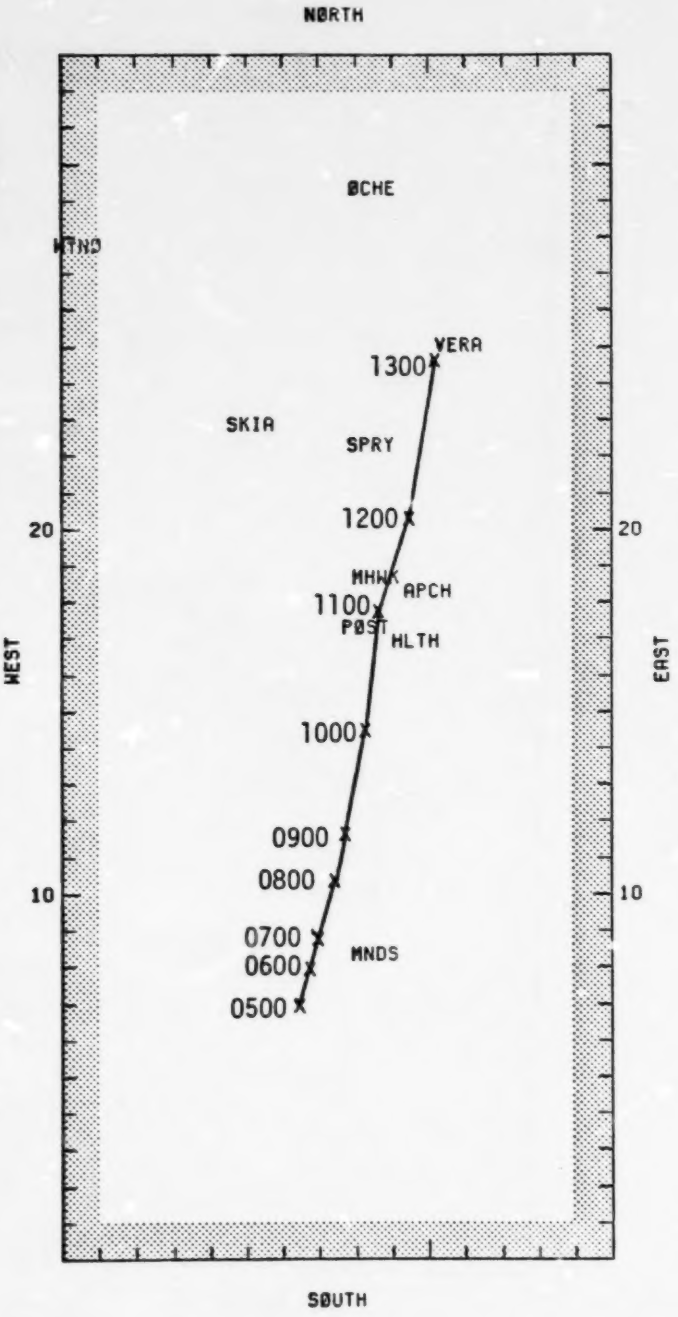
On the basis of the results of the SAI trajectory model, emissions and meteorological conditions are constructed for a Level II type of EKMA model using Carbon-Bond chemistry and a Level II EKMA based on the standard propylene/butane chemistry as used in the original version of the OZIPP code.

The SAI trajectory model prints out the emissions and mixing heights along the trajectory path at hourly intervals. These mixing heights can be used as direct inputs to the OZIPM computer code. The emissions rates from the SAI trajectory model are in units of moles/hr for each of the Carbon-Bond species. These emissions are converted to ppmC/hr for volatile organic compounds (VOC) by the following equation:

$$\text{Emissions Rate (ppmC/hr)} = [24450/(Z_0 * 4000^2)][\text{Emissions Rate (moles/hr)}] ,$$

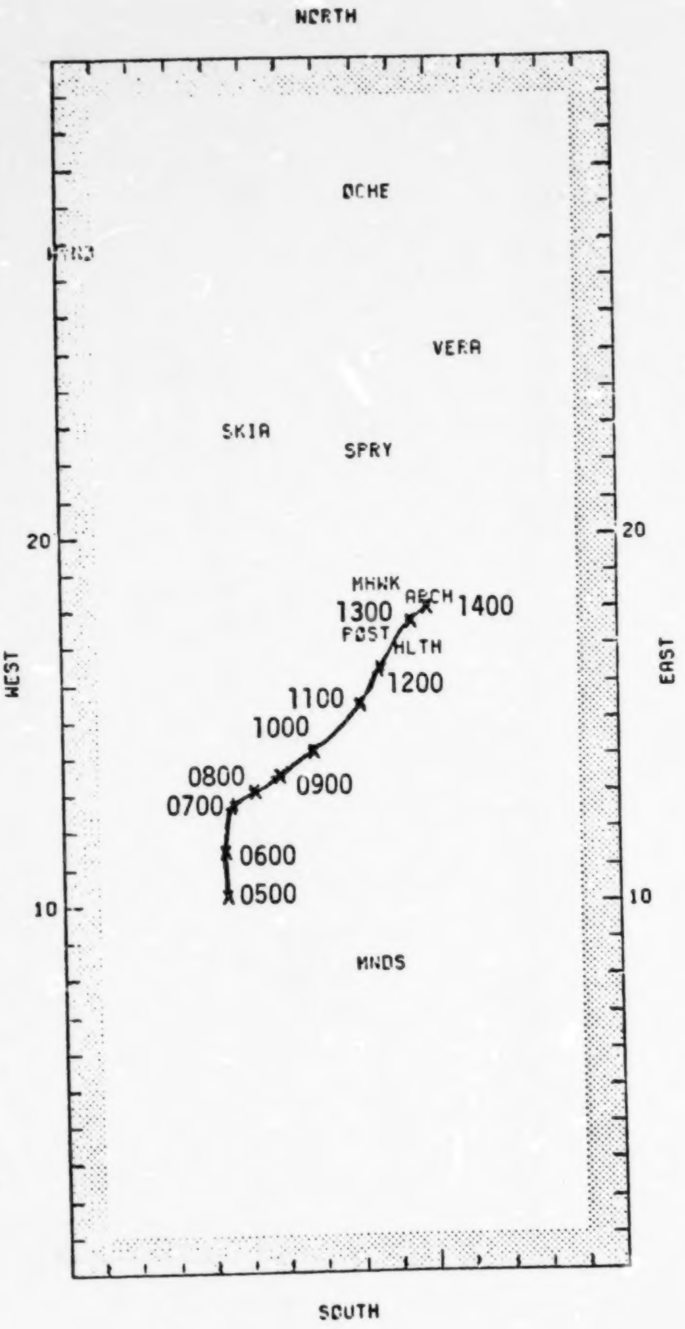
where Z_0 is the initial mixing height.

Initial NO_x and VOC precursors (OZIPM) are taken from the initial conditions from the average of the layers below the mixing height found in the SAI trajectory model. NO_x and VOC precursors aloft are determined from the amount of precursors that entered the mixed layer from aloft in the SAI trajectory model simulations. As a result of using this methodology, the NO_x and VOC aloft precursors are usually higher than measured values. The chemistry in the SAI trajectory model will produce secondary organic products (such as carbonyls) and ozone in the layer aloft. Thus, if we were to compare assumed aloft conditions in the CBM/OZIPM (tables 3-3 through 3-6) and actual measured data, we would find higher concentrations in the OZIPM models. This method was used because the species aloft continuously react in the SAI trajectory model, whereas OZIPM does not treat precursors aloft until they are entrained. Emissions and meteorological conditions for the four modeling days are shown in tables 3-3 through 3-6.



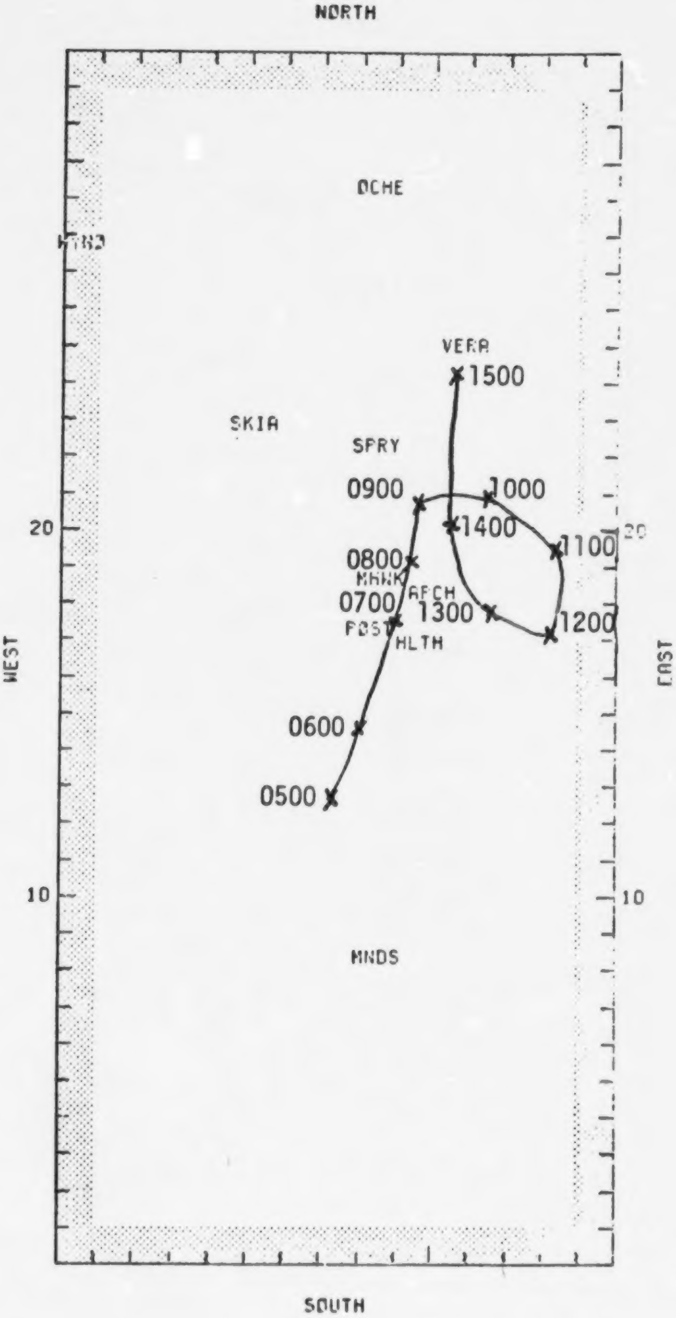
(a) For 21 July 1977

Figure 3-5. Trajectory path (CDT).


NORTH
OCHE
VERA
SKIA
SPRY
20
20
MHWK
ARCH
1300
1400
FOST
HLTH
1200
1100
1000
0800
0900
0700
0600
0500
10
10
MNDS
WEST
EAST
SOUTH

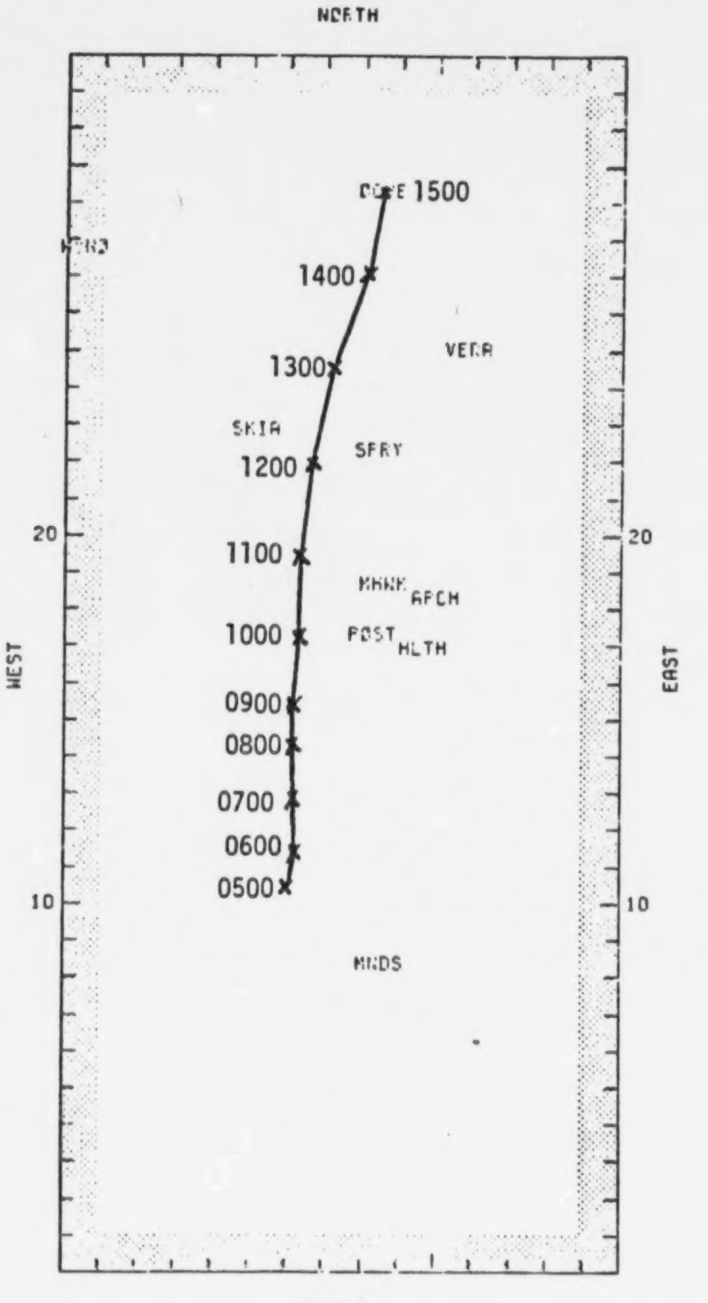
(b) For 29 July 1977

Figure 3-5 (Continued).


NORTH
OCHE
WTRD
VERA
1500
SKIA
SPRY
0900
1000
1400
20
1100
20
0800
MAWK
ARCH
0700
1300
FOST
HLTH
1200
WEST
EAST
0600
0500
10
10
MNDS
SOUTH

(c) For 3 August 1977

Figure 3-5 (Continued).



(d) For 2 September 1977

Figure 3-5 (Concluded).

49r 81 18

TABLE 3-3. INITIAL CONDITIONS AND EMISSIONS RATES USED IN THE LEVEL II CBM/OZIPM CALCULATIONS FOR 21 JULY 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.003 ppm	0.003 ppm
NMOC	0.163 ppmC	0.13 ppmC
O_3	0.0356 ppm	0.067 ppm

NO_2/NO_x = 0.916.

Hydrocarbon reactivity:

OLE = 0.018
PAR = 0.826
ARO = 0.121
ETH = 0.016
CARB = 0.009

(b) Emissions Rates and Mixing Heights

Time (CDT)	Species		Mixing Height at the Beginning of Each Hour (m)
	VOC (ppmC/hr)	NO_x (ppm/hr)	
0500-0600	0.0002	0.0009	50
0600-0700	0.0004	0.0037	50
0700-0800	0.0024	0.1294	50
0800-0900	0.0058	0.0573	50
0900-1000	0.0144	0.0513	100
1000-1100	1.2202	0.118	200
1100-1200	0.0723	0.3333	450
1200-1300	0.0137	0.0367	600
1300-1400	0.0041	0.0113	600
1400-1500	0.0014	0.0043	600
1500			700

TABLE 3-4. INITIAL CONDITIONS AND EMISSIONS RATES USED IN THE CBM/OZIPM CALCULATIONS FOR 29 JULY 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0036 ppm	0.0016 ppm
NMOC	0.1356 ppmC	0.1066 ppmC
O_3	0.0326 ppm	0.0826 ppm

$NO_2/NO_x = 0.997$.

Hydrocarbon reactivity:

OLE = 0.0409
PAR = 0.7886
ARO = 0.1296
ETH = 0.0320
CARB = 0.0089

(b) Emissions Rates and Mixing Heights

Time (CDT)	Species		Mixing Height at the Beginning of Each Hour (m)
	VOC (ppmC/hr)	NO_x (ppm/hr)	
0500-0600	0.0007	0.0002	50
0600-0700	0.0026	0.0007	50
0700-0800	0.0112	0.0031	50
0800-0900	0.0373	0.0076	50
0900-1000	0.0312	0.0076	100
1000-1100	0.1265	0.0340	200
1100-1200	1.4423	0.1751	300
1200-1300	0.8083	0.1949	600
1300-1400	0.3448	0.0766	700
1400			900

TABLE 3-5. INITIAL CONDITIONS AND EMISSIONS RATES USED IN THE CBM/OZIPM CALCULATIONS FOR 3 AUGUST 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0323 ppm	0.0034 ppm
NMOC	0.2035 ppmC	0.1125 ppmC
O_3	0.0109 ppm	0.0702 ppm

$NO_2/NO_x = 0.999$.

Hydrocarbon reactivity:

OLE = 0.0416
PAR = 0.7819
ARO = 0.1416
ETH = 0.0282
CARB = 0.0067

(b) Emissions Rates and Mixing Heights

Time (CDT)	Species		Mixing Height at the Beginning of Each Hour (m)
	VOC (ppmC/hr)	NO_x (ppm/hr)	
0500-0600	0.0098	0.0035	50
0600-0700	0.8317	0.0995	50
0700-0800	0.1633	0.0464	50
0800-0900	0.0610	0.0219	50
0900-1000	0.0335	0.0098	50
1000-1100	0.0240	0.0121	100
1100-1200	0.00	0.00	180
1200-1300	0.0632	0.0243	260
1300-1400	0.0866	0.0302	540
1400-1500	0.0220	0.0069	680
1500			800

TABLE 3-6. INITIAL CONDITIONS AND EMISSIONS RATES USED IN THE CBM/OZIPM CALCULATIONS FOR 2 SEPTEMBER 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0065 ppm	0.0021 ppm
NMOC	0.2034 ppmC	0.1033 ppmC
O_3	0.0281 ppm	0.0712 ppm

NO_2/NO_x = 0.9985.

Hydrocarbon reactivity:

OLE = 0.0364
PAR = 0.6913
ARO = 0.1610
ETH = 0.0845
CARB = 0.0268

(b) Emissions Rates and Mixing Heights

Time (CDT)	Species VOC (ppmC/hr)	 NO_x (ppm/hr)	Mixing Height at the Beginning of Each Hour (m)
0500-0600	0.0054	0.0001	50
0600-0700	0.0113	0.0027	50
0700-0800	0.0273	0.0071	50
0800-0900	0.0264	0.0085	50
0900-1000	0.1616	0.0277	50
1000-1100	0.0288	0.0037	100
1100-1200	0.0017	0.00	100
1200-1300	0.0021	0.0003	600
1300-1400	0.0020	0.0004	1000
1400-1500	0.0031	0.0003	1000
1500			1000

For the Level II EKMA using propylene/butane chemistry, the standard default reactivity of 25 percent propylene and 75 percent butane was used along with the emissions and meteorological inputs discussed previously.

INPUTS USED IN THE LEVEL III EKMA MODEL SIMULATIONS

Emissions and meteorological inputs were developed as outlined in the EPA (1980) guidelines document. All assumptions made for this study are based on that document, which was in draft form during this study.

There are six input options available in the standard OZIPP Model (light intensity, dilution, ozone transport, precursor transport, post-0800 emissions, and reactivity). Emissions inventories for the Tulsa study developed by Engineering Science (1980) were reported for each county located in the study region. The county-wide emissions are presented in table 3-7 along with the land area of each county. The NO_x and VOC emissions in units of kg/yr are converted to emissions densities in units of kg/hr km^2 (table 3-8).

Straight-line trajectories from the urban core to the location of the maximum observed ozone were drawn and are shown in figure 3-6(a) through 3-6(d). As seen in these figures, the maximum observed ozone usually occurred near Tulsa County for the four days.

Morning and afternoon mixing heights were determined from upper air soundings taken at the airport (as discussed in appendix A). The initial conditions used in the Level III EKMA calculations are presented in tables 3-9 through 3-12. Urban average 0600 to 0900 ambient concentrations of NMOC and NO_x are reported by Eaton et al. (1979a). Two monitoring stations (Tulsa post office and health department) are located in the urban core. The reported 0600 to 0900 NMOC and NO_x concentrations from these two stations were averaged and used to determine the post-0800 emissions fractions used in the Level III EKMA calculations for the four modeling days. Ozone transport for each day was determined from observations made at the Liberty Mounds station located 37 km south of the urban core. Eaton et al. (1979b) reported that the Liberty Mounds station was influenced by the urban core 14 days out of the three-month study period. Thus, Liberty Mounds represents the upwind station for the four modeling days. Although NMOC and NO_x precursors are not considered in this section, on the basis of recommendations in the Level III guidelines, the effects of using NMOC and NO_x precursors (surface and aloft) in the EKMA calculations are examined in section 6.

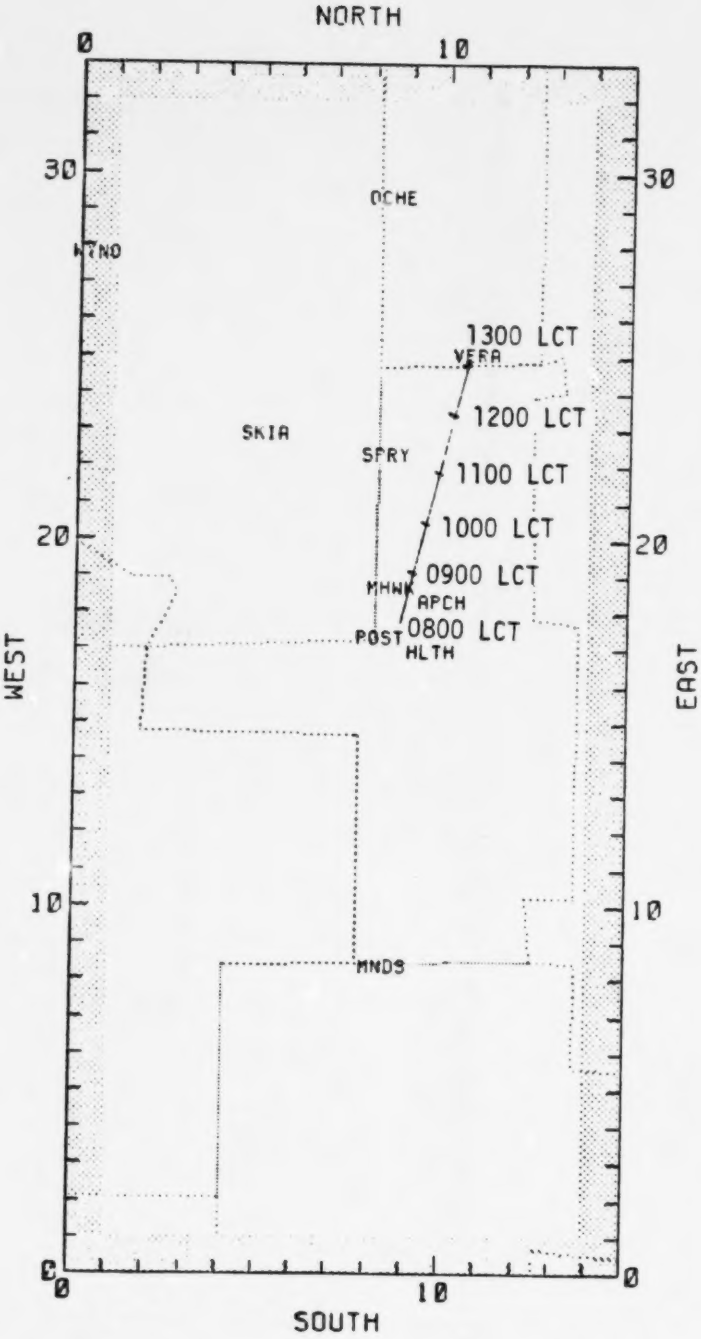
The assumed ozone concentrations aloft for each day were based on the analysis by Eaton et al. (1979b), which compared aircraft measurements

TABLE 3-7. COUNTY-WIDE EMISSIONS ESTIMATES FOR 1977

County	Area (km^2)	Emissions (kg/yr)	
		NMOC	NO_x
Tulsa	1.48×10^3	5.08×10^7	4.96×10^7
Washington	1.10×10^3	5.98×10^5	5.97×10^5
Creek	2.42×10^3	1.94×10^6	9.82×10^5
Osage	5.88×10^3	1.06×10^6	5.24×10^5
Okmulgee	1.81×10^3	4.65×10^6	1.27×10^6

TABLE 3-8. CALCULATED EMISSIONS DENSITY FOR FIVE OKLAHOMA CITIES

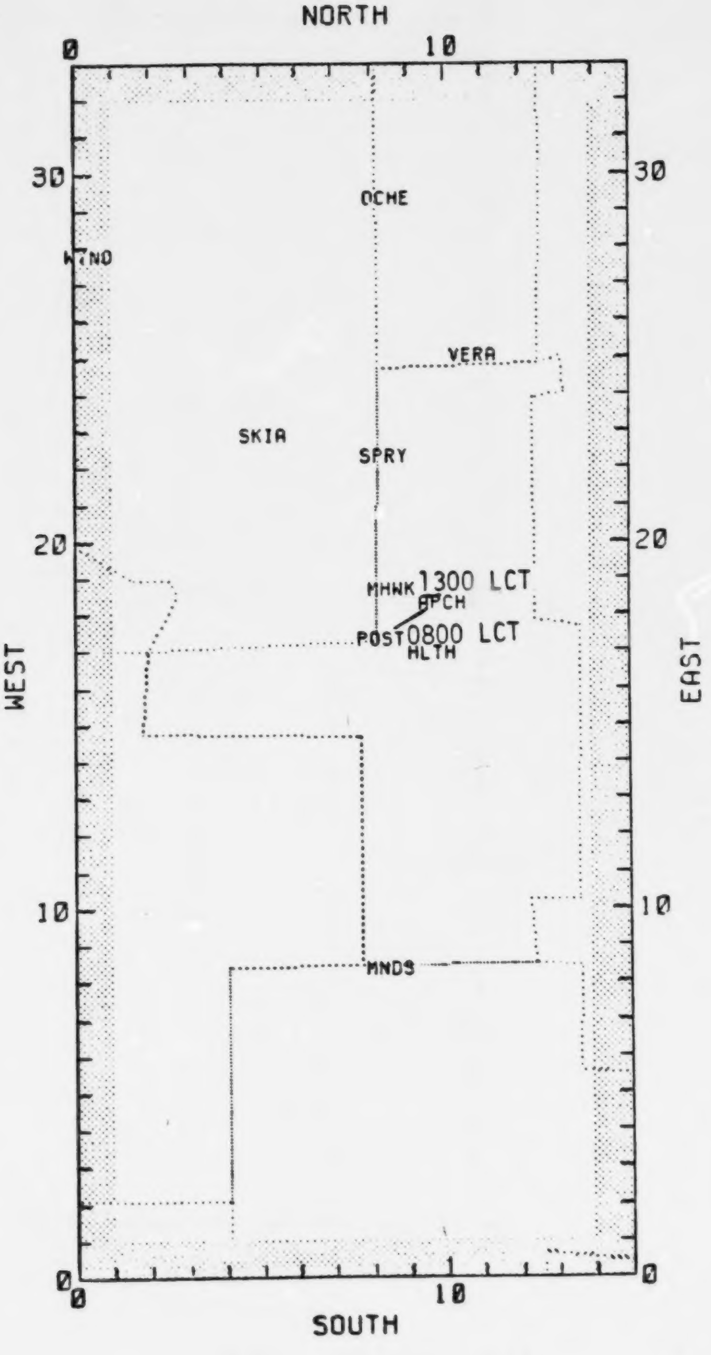
County	Emissions ($kg/hr\ km^2$)	
	NMOC	NO_x
Tulsa	3.92	3.83
Washington	0.0621	0.062
Creek	0.0915	0.0463
Osage	0.0206	0.0102
Okmulgee	0.293	0.0801


NORTH
0
10
30
30
OCHE
WTNO
1300 LCT
VERA
1200 LCT
SKIA
SPRY
1100 LCT
1000 LCT
20
20
0900 LCT
MHWK
APCH
0800 LCT
POST
HLTH
WEST
EAST
10
10
MNDS
0
0
0
10
SOUTH

LCT = local civil time.

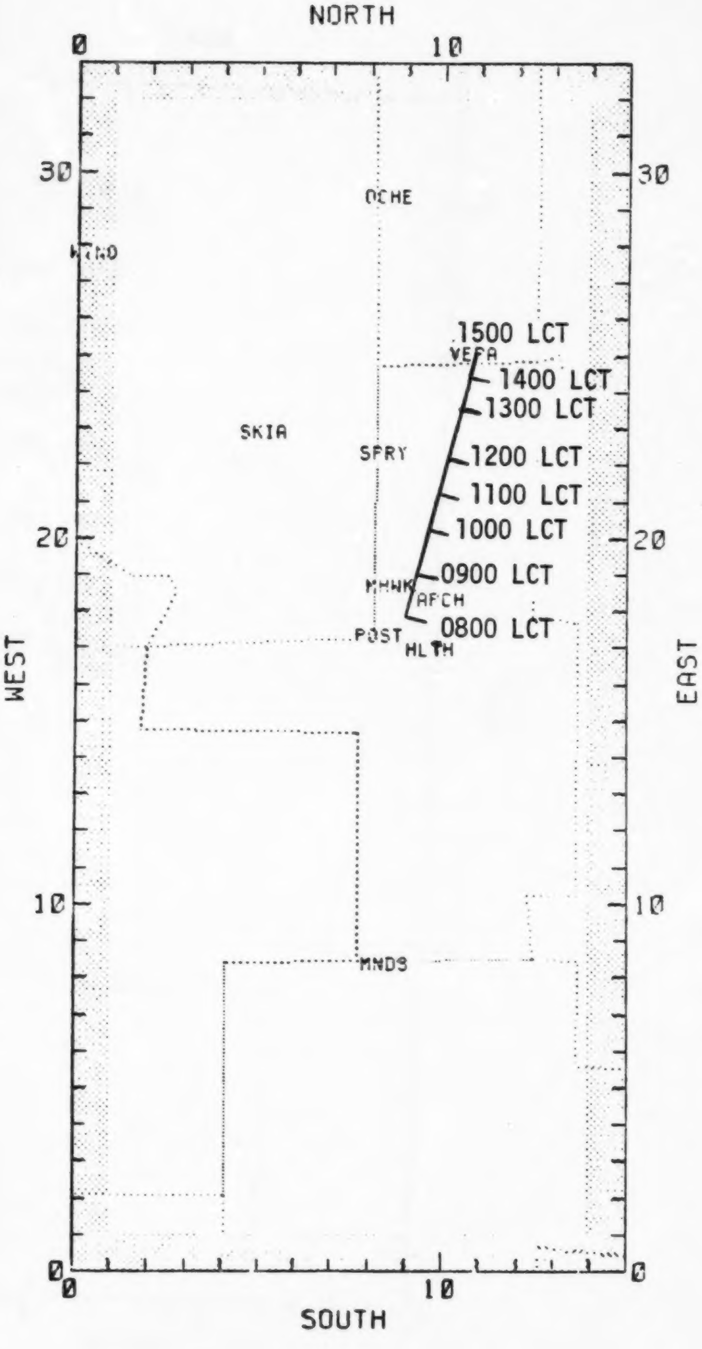
(a) For 21 July 1977

Figure 3-6. Level III straight-line trajectory to maximum O_3.


NORTH
0
10
30
20
10
0
OCHE
WIND
VERA
SKIA
SPRY
MHWK
1300 LCT
APCH
POST
0800 LCT
HLTH
MNDS
WEST
EAST
SOUTH

(a) For 29 July 1977

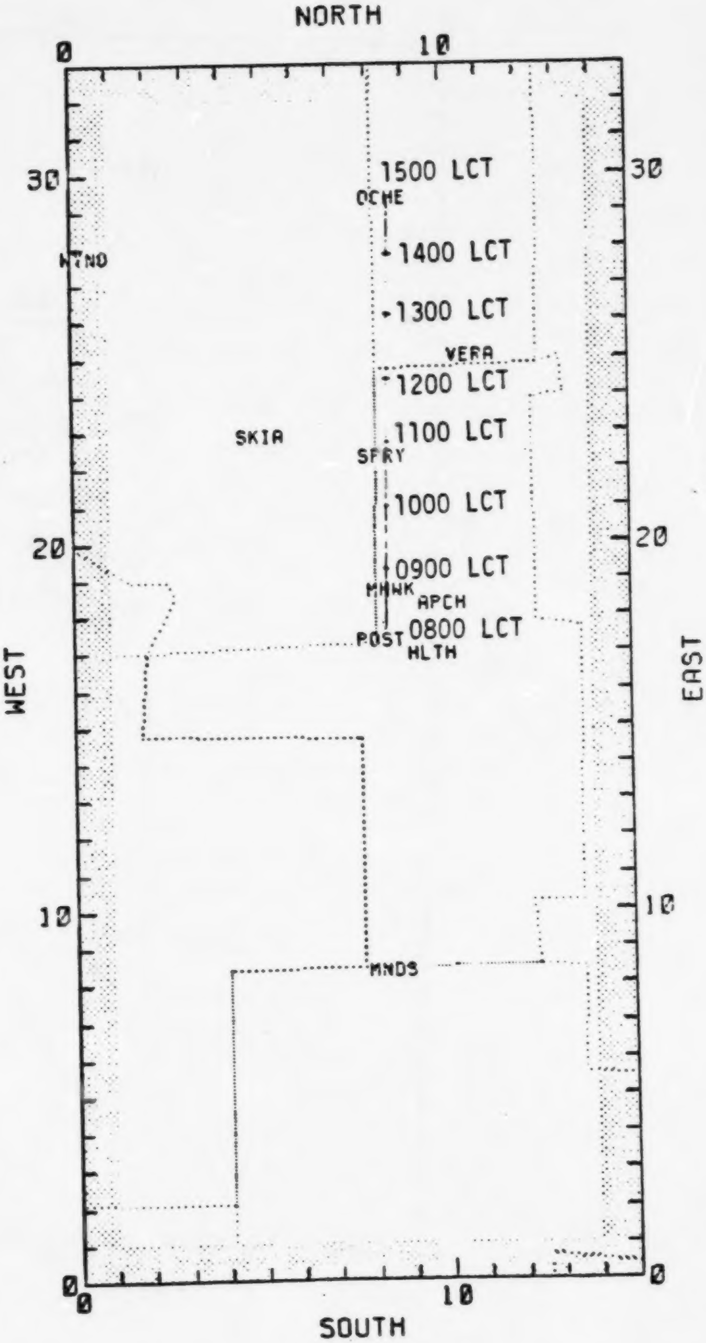
Figure 3-6 (continued).


NORTH
0
10
30
20
10
0
WEST
EAST
SOUTH
OCHE
WIND
SKIA
SPRY
VEFA
1500 LCT
1400 LCT
1300 LCT
1200 LCT
1100 LCT
1000 LCT
0900 LCT
MHWK
AFCH
0800 LCT
POST
HLTH
MNDS

(c) For 3 August 1977

Figure 3-6 (continued).

49r 81 18


NORTH
0
10
30
20
10
0
WEST
EAST
SOUTH
1500 LCT
OCHE
1400 LCT
1300 LCT
VERA
1200 LCT
1100 LCT
SKIA
SFRY
1000 LCT
0900 LCT
MHWK
APCH
0800 LCT
POST
HLTH
NTNO
MNDS

(c) For 2 September 1977

Figure 3-6 (concluded).

49r 81 1 8

TABLE 3-9. INITIAL CONDITIONS USED IN THE LEVEL III EKMA CALCULATIONS FOR 21 JULY 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0 ppm	0.0 ppm
NMOC	0.0 ppmC	0.0 ppmC
O_3	0.0 ppm	0.07 ppm

NO_2/NO_x = 0.25.

Hydrocarbon reactivity: standard OZIPP conditions.
Morning mixing height: 150 m at 0800 CDT.
Afternoon mixing height 600 m at 1200 CDT.
$NMOC/NO_x$ at 0600 to 0900 CDT = 6.15.
NMOC at 0600 to 0900 CDT = 0.283 ppmC.
NO_x at 0600 to 0900 CDT = 0.046 ppm.
Design O_3 = 0.14 ppm at Vera (1300 CDT).

(b) Emissions Fractions

Time (CDT)	NMOC	NO_x
0800-0900	0.155	0.294
0900-1000	0.155	0.294
1000-1100	0.155	0.294
1100-1200	0.155	0.294
1200-1300	0.079	0.150

TABLE 3-10. INITIAL CONDITIONS USED IN THE LEVEL III EKMA CALCULATIONS FOR 29 JULY 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0 ppm	0.0 ppm
NMOC	0.0 ppmC	0.0 ppmC
O_3	0.0 ppm	0.08 ppm

$NO_2/NO_x = 0.25$.

Hydrocarbon reactivity: standard OZIPP conditions.
Morning mixing height: 150 m at 0800 CDT.
Afternoon mixing height: 900 m at 1400 CDT.
$NMOC/NO_x$ at 0600 to 0900 CDT = 9.09.
NMOC at 0600 to 0900 CDT = 0.482 ppmC.
NO_x at 0600 to 0900 CDT = 0.053 ppm.
Design O_3 = 0.147 ppm at Apache (1400 CDT).

(b) Emissions Fractions

Time (CDT)	NMOC	NO_x
0800-0900	0.091	0.255
0900-1000	0.091	0.255
1000-1100	0.091	0.255
1100-1200	0.091	0.255
1200-1300	0.091	0.255
1300-1400	0.091	0.255

TABLE 3-11. INITIAL CONDITIONS USED IN THE LEVEL III EKMA CALCULATIONS FOR 3 AUGUST 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0 ppm	0.0 ppm
NMOC	0.0 ppmC	0.0 ppmC
O_3	0.0 ppm	0.09 ppm

$NO_2/NO_x = 0.25$.

Hydrocarbon reactivity: standard OZIPP conditions.
Morning mixing height: 150 m at 0800 CDT.
Afternoon mixing height 800 m at 1500 CDT.
$NMOC/NO_x$ at 0600 to 0900 CDT = 12.1.
NMOC at 0600 to 0900 CDT = 0.598 ppmC.
NO_x at 0600 to 0900 CDT = 0.05 ppm.
Design O_3 = 0.15 ppm at Vera (1500 CDT).

(b) Emissions Fractions

Time (CDT)	NMOC	NO_x
0800-0900	0.074	0.270
0900-1000	0.074	0.270
1000-1100	0.074	0.270
1100-1200	0.074	0.270
1200-1300	0.074	0.270
1300-1400	0.074	0.270
1400-1500	0.037	0.138

TABLE 3-12. INITIAL CONDITIONS USED IN THE LEVEL III EKMA CALCULATIONS FOR 2 SEPTEMBER 1977

(a) Initial Conditions

Species	Surface	Aloft
NO_x	0.0 ppm	0.0 ppm
NMOC	0.0 ppmC	0.0 ppmC
O_3	0.0 ppm	0.07 ppm

NO_2/NO_x = 0.25.

Hydrocarbon reactivity: standard OZIPP conditions.
Morning mixing height: 150 m at 0800 CDT.
Afternoon mixing height 1000 m at 1300 CDT.
$NMOC/NO_x$ at 0600 to 0900 CDT = 8.75.
NMOC at 0600 to 0900 CDT = 0.52 ppmC.
NO_x at 0600 to 0900 CDT = 0.059 ppm.
Design O_3 = 0.11 ppm at Ochelata (1500 CDT).

(b) Emissions Fractions

Time (CDT)	NMOC	NO_x
0800-0900	0.085	0.229
0900-1000	0.085	0.229
1000-1100	0.085	0.229
1100-1200	0.085	0.229
1200-1300	0.043	0.117
1300-1400	0.0013	0.004
1400-1500	0.0013	0.004

with the ground-level ozone measurements. Eaton reported that in most cases, aircraft measurements of ozone are higher than the ozone measurements at the surface. For two of the aircraft measurement days, the difference between the airborne ozone measurements and the Liberty Mounds measurements was less than 0.01 ppm. On both of these days, the measured wind speeds at the health department during the time of the aircraft measurements were greater than 13 mph. On the other aircraft measurement days, the differences in ozone concentration between the aircraft and surface measurements were in excess of 0.03 ppm. The wind speeds measured at the health department were 6 mph or less.

For the Level III EKMA inputs, we based the ozone concentration values aloft on the findings by Eaton. We expected that, at a minimum, these concentrations would be greater than the 1100 to 1300 CDT Liberty Mounds measurements by about 0.02 ppm and set the aloft ozone values accordingly. For 3 August we kept the ozone aloft value equal to the surface observations since the wind speeds at Liberty Mounds were fairly high for this day compared with the other days.

To study the differences between the propylene/butane chemistry currently employed in the EKMA with the Carbon-Bond chemistry, we replaced the propylene/butane chemistry with the Carbon-Bond Mechanism without making any other changes to emissions and meteorological inputs. A default reactivity similar to the default 25 percent propylene reactivity of the standard OZIPP chemistry was used in all the Level III EKMA/CBM calculations. The following reactivities were taken from Killus and Whitten (1981):

OLE	0.03
PAR	0.65
ARO	0.22
ETH	0.05
CARB	0.05.

SECTION 4

COMPARISON OF MODEL RESULTS

This section presents a comparison of the absolute predictions for each of the models discussed in the previous chapters. In almost all cases, these models use meteorological and emissions inputs discussed in section 3; specific exceptions are noted at the time of their discussion. A summary of the ozone predictions for the four models is presented in table 4-1.

SAI AIRSHED MODEL RESULTS

Ozone predictions and model performance for the SAI Airshed Model have been discussed in detail by Reid, Reynolds, and Latimer (1980). We wish to summarize here some of these performance evaluations for the four modeling days. Table 4-2 presents the effects of some of the performance measures on peak ozone concentrations. These measures were based on comparisons of the maximum observed concentrations with the highest value computed at a particular monitoring station even though the two values may not have occurred at the same time.

As shown in table 4-2, both the median deviation and mean deviations for 21 July 1973 are less than 0.01 ppm, indicating little bias in the results. Since the median and mean absolute deviations are less than 0.015 ppm, the gross error in the peak predictions is also small. When the absolute deviation is normalized by the measured value, we find that the median and mean discrepancy between the computed and observed peak concentrations is 14 and 19 percent, respectively. The ratio of peak computed to peak measured concentrations can also be considered; the median and mean values for this comparison are 0.99 and 0.94, respectively, as indicated in table 4-2.

In table 4-2, we also see that the highest measured and predicted ozone concentrations differ by less than 0.01 ppm for 29 July 1977. Although little bias is indicated in table 4-2 for this day, the gross error in predictions is slightly higher than that for 21 July 1977. For 3 August 1977, the Airshed Model tended to underpredict ozone, as shown by

TABLE 4-1. COMPARISON OF OZONE PREDICTIONS FOR THE SAI AIRSHED, SAI TRAJECTORY, LEVEL II, AND LEVEL III EKMA MODELS--1977

(ppm)

Model	Ozone Level 21 July (Obs[*] O_3=0.14)	29 July (Obs O_3=0.17)	3 Aug (Obs O_3=0.15)	2 Sept (Obs O_3=0.11)
SAI Airshed	0.14	0.17	0.12	0.12
SAI Trajectory	0.15	0.14	0.15	0.09
Level II EKMA	0.10	0.11	0.10	0.08
Level II w/CBM[†]	0.15	0.14	0.15	0.09
Level III EKMA	0.10	0.12	0.13	0.10
Level III w/CBM[§]	0.12	0.15	0.18	0.13

---

[*] OBS = observed.

[†] BZA and PAN entrained from aloft are used (see the text for further discussion).

[§] CBM (Carbon-Bond chemistry).

TABLE 4-2. SUMMARY OF PEAK OZONE CONCENTRATION MODEL PERFORMANCE EVALUATION MEASURES

Performance Measure	21 July*	29 July*	3 August*	2 September*
Highest observed value at peak station*	0.135	0.166	0.151	0.108
Highest computed value at peak station	0.135	0.174	0.115	0.120
Highest computed value at any station	0.135	0.174	0.143	0.128
Highest computed ground-level value on the grid	0.14	0.21	0.16	0.13
Deviation for all stations				
Median	-0.003	-0.006	-0.007	0.011
Mean	-0.006	-0.002	-0.010	0.012
Standard deviation	0.021	0.024	0.029	0.019
N†	10	10	10	10
Deviation for all stations with observed value > 0.12 ppm				
Median	0.000	0.008	-0.014	--
Mean	0.000	0.010	-0.024	--
Standard deviation	--	0.041	0.025	--
N†	1	3	5	0
Normalized deviation for all stations				
Median	0.01	-0.06	-0.04	0.10
Mean	-0.06	0.01	-0.07	0.18
Standard deviation	0.26	0.22	0.26	0.28
N†	10	10	10	10

TABLE 4-2 (Continued)

Performance Measure	21 July*	29 July*	3 August*	2 September*
Normalized deviation for all stations with observed value > 0.12 ppm				
Median	0.00	-0.24	-0.12	--
Mean	0.00	0.08	-0.19	--
Standard deviation	--	0.11	0.20	--
N†	1	3	5	0
Absolute deviation for all stations				
Median	0.012	0.014	0.021	0.016
Mean	0.015	0.018	0.022	0.018
Standard deviation	0.015	0.015	0.020	0.011
N†	10	10	10	10
Absolute deviation for all stations with observed value > 0.12 ppm				
Median	0.000	0.030	0.014	--
Average	0.000	0.030	0.025	--
Standard deviation	--	0.022	0.024	--
N†	1	3	5	0
Normalized absolute deviation for all stations				
Median	0.14	0.16	0.18	0.22
Average	0.19	0.17	0.20	0.26
Standard deviation	0.18	0.12	0.17	0.19
N†	10	10	10	10
Normalized absolute deviation for all stations with observed value > 0.12 ppm				
Median	0.00	0.24	0.12	--
Average	0.00	0.24	0.19	--
Standard deviation	--	0.19	0.20	--
N†	1	3	5	0

TABLE 4-2 (Concluded)

Performance Measure	21 July[*]	29 July[*]	3 August[*]	2 September[*]
Ratio of highest computed value to highest observed value at each station				
Median	0.99	0.92	1.01	1.11
Average	0.94	0.96	0.93	1.18
Standard deviation	0.26	0.26	0.21	0.28
N[†]	10	10	10	10
Ratio of highest computed value to highest observed value at all stations with observed value > 0.12 ppm				
Median	1.00	1.05	0.88	--
Average	1.00	1.08	0.81	--
Standard deviation	--	0.34	0.20	--
N[†]	1	3	5	0
Correlation coefficient for all stations	0.71	0.84	0.22	0.63

---

[*] All concentration values are expressed as ppm.

[†] N refers to the number of comparisons.

the median and mean deviation for all stations with observed ozone values greater than 0.12 ppm. The gross error (reflected in the normalized median and average deviations) is higher for 3 August than for either 21 July or 29 July and is even higher for 2 September.

The bias in model predictions can be examined by computing the mean deviation and mean normalized deviation of hourly pairs of predicted and observed concentrations. The results of this exercise are presented in table 4-3 for all four modeling days. For the 21 July 1977 day, the model tended to underestimate ozone levels by about 17 percent. Considering only those comparisons for which the measured value exceeded 0.12 ppm, we found that the model showed a tendency to overpredict by about 4 percent. For 29 July 1977 and 3 August 1977, the model tended to underpredict ozone by 14 and 23 percent, respectively, for all measured ozone and by 20 and 22 percent, respectively, for measured ozone values greater than 0.12 ppm. In contrast, the model tended to overestimate measured ozone by 8 percent for 2 September 1977 (an attainment day).

COMPARISON OF SAI AIRSHED AND SAI TRAJECTORY MODEL RESULTS

As discussed in section 3, the SAI Airshed and SAI trajectory models use the same meteorological and emissions inputs. However, the SAI trajectory model is a two-dimensional model that uses only the first vertical level of winds to describe the specific trajectory path. The trajectory model follows the path of an air column the size of a single grid cell using the same computer codes as the Airshed Model except for those that involve horizontal dispersion, vertical winds, and wind shear. We expect the SAI Airshed and SAI trajectory models to predict similar ozone values for those days with low vertical winds and wind shear. However, the SAI trajectory model could also predict results similar to the SAI Airshed Model for those modeling days with high wind shear. This could be coincidental if the emissions densities are evenly distributed spatially or if the three-dimensional path of the air parcel in the Airshed Model never passes over an area with high emission peaks. Thus, SAI trajectory model results need to be analyzed in detail to understand discrepancies with SAI Airshed predictions.

The SAI trajectory model results shown in table 4-1 for the four modeling days were obtained without incorporating surface sinks. Such results are more comparable with the CBM/OZIPM EKMA results discussed later. The use of surface sinks can lead to a 10 to 15 percent reduction in ozone predictions over those of the SAI models. Therefore, we expect the trajectory model to predict higher ozone values than the Airshed Model. For 21 July 1977, the SAI trajectory model predicted a maximum ozone concentration of 0.138 ppm when surface sinks were used, and a value

45 r 81 18

TABLE 4-3. SUMMARY OF SAI AIRSHED MODEL PERFORMANCE EVALUATION MEASURES

Performance Attribute	Performance Measure	21 July 1977		29 July 1977	
		Value for Measured $O_3 > 0.02$ ppm	Value for Measured $O_3 > 0.12$ ppm	Value for Measured $O_3 > 0.02$ ppm	Value for Measured $O_3 > 0.12$ ppm
Absence of systematic bias	Mean deviation				
	Normalized--				
	Average	-0.17	0.04	-0.14	-0.20
	Std. dev.	0.38	0.04	0.29	0.24
	Nonnormalized--				
	Average	-0.007 ppm	0.005 ppm	-0.010 ppm	-0.028 ppm
	Std. dev.	0.017 ppm	0.005 ppm	0.022 ppm	0.035 ppm
Lack of gross error	Mean absolute deviation				
	Normalized--				
	Average	0.33	0.04	0.27	0.27
	Std. dev.	0.26	0.04	0.17	0.14
	Nonnormalized--				
	Average	0.015 ppm	0.005 ppm	0.019 ppm	0.039 ppm
	Std. dev.	0.011 ppm	0.005 ppm	0.014 ppm	0.021 ppm
Temporal correlation	Temporal correlation coefficients--				
	Each station	0.71 to 0.98	--	0.36 to 0.92	0.43
	All-station average	0.87	--	0.82	0.43
Spatial alignment	Spatial correlation coefficients--				
	Each hour	-0.38 to 0.84	--	-0.47 to 0.87	--
	All-hour average	0.38	--	0.51	--
N*		135	3	137	8

---

* Number of pairs of computed and measured values.

49r 81 18

TABLE 4-3 (Concluded)

Performance Attribute	Performance Measure	3 August 1977 Value for Measured $O_3 > 0.02$ ppm	3 August 1977 Value for Measured $O_3 > 0.12$ ppm	2 September 1977 Value for Measured $O_3 > 0.02$ ppm	2 September 1977 Value for Measured $O_3 > 0.12$ ppm
Absence of systematic bias	Mean deviation				
	Normalized--				
	Average	-0.23	-0.22	0.08	--
	Std. dev.	0.37	0.15	0.36	--
	Nonnormalized--				
	Average	-0.017 ppm	-0.029 ppm	0.005 ppm	--
	Std. dev.	0.024 ppm	0.018 ppm	0.018 ppm	--
Lack of gross error	Mean absolute deviation				
	Normalized--				
	Average	0.36	0.22	0.27	--
	Std. dev.	0.24	0.15	0.24	--
	Nonnormalized--				
	Average	0.025 ppm	0.029 ppm	0.014 ppm	--
	Std. dev.	0.015 ppm	0.018 ppm	0.012 ppm	--
Temporal correlation	Temporal correlation coefficients--				
	Each station	0.63 to 0.98	--	0.61 to 0.91	--
	All-station average	0.85	--	0.80	--
Spatial alignment	Spatial correlation coefficients--				
	Each hour	-0.50 to 0.53	--	-0.34 to 0.87	--
	All-hour average	0.16	--	0.51	--
N*		116	7	113	

---

* Number of pairs of computed and measured values.

of 0.154 ppm (table 4-1) without the use of surface sinks. This ozone value of 0.138 ppm compares very well with the SAI Airshed Model prediction of 0.14 ppm.

For 29 July 1977, the trajectory model ozone prediction of 0.14 ppm (without surface sinks) was approximately 17.5 percent lower than the SAI Airshed Model prediction of 0.17 ppm. Since wind data for 29 July show high wind shear within the mixed layer during the morning hours, we cannot conclude that the trajectory path to the maximum ozone concentration was similar to that followed in the Airshed Model simulations for the air arriving at the point of maximum ozone. Section 6 discusses methods of determining alternative trajectory paths for this modeling day in place of the use of surface winds only. We note that trajectory paths to cells adjacent to the cell in which the monitoring station is located show wide variations in ozone predictions. An ozone maximum of 0.17 ppm was found in the cell just northeast of the cell that contained the monitoring station.

For 3 August 1977, the ozone value predicted by the SAI trajectory model was 25 percent higher than the 0.12 ppm ozone value predicted by the Airshed Model, apparently because surface sinks were not incorporated in the trajectory model simulation.

For 2 September 1977, the SAI trajectory model predicted lower ozone concentrations than the Airshed Model, even though no surface sinks were used in the trajectory model simulation. Investigation of the wind fields used in the Airshed Model within the mixed layer showed some shear during the early-morning hours. The first-level wind field showed low speeds, but the second-level winds were, on the average, twice as fast (with a 10° difference in direction).

COMPARISON OF SAI TRAJECTORY AND LEVEL II EKMA MODEL RESULTS

This section is divided into two parts: the first presents a discussion of the predictions from the SAI trajectory model and the Level II EKMA with Carbon-Bond Chemistry (CBM/OZIPM). The second presents a comparison of ozone predictions for the Level II EKMA using propylene/-butane chemistry with those of the CBM/OZIPM.

Although the results shown in table 4-1 for the SAI trajectory model and the CBM/OZIPM are in close agreement, it was necessary to consider entrainment of BZA and PAN (two species in the Carbon-Bond Mechanism) from aloft. When we first began CBM/OZIPM calculations using the inputs described in section 3, we found the CBM/OZIPM predictions consistently low when compared with ozone predicted by the SAI trajectory model.

Although the CBM/OZIPM predictions were within 10 percent of the SAI trajectory model, we felt that the CBM/OZIPM could provide better agreement. Detailed investigations of the predicted concentration profiles from the SAI trajectory model and the CBM/OZIPM model indicated a major discrepancy in BZA and PAN predictions between the two models. Upon reexamination of the chemistry and the meteorological conditions for the four modeling days, we discovered that the introduction of BZA and PAN into the mixed layer from aloft was an important factor in the SAI trajectory model simulations. The amounts of BZA and PAN simulated aloft for these four modeling days are presented in table 4-4. The multilayer SAI trajectory model continuously simulates the chemistry in each layer. At any instant in time during the daylight hours, some of the overall reactivity of an air parcel is contained in intermediate species, which are equilibrated with the reacting system of sunlight and precursors, such as PAN and BZA. Failure to entrain such simulated intermediates from aloft necessitates the use of some reactivity within the mixed layer to replace these intermediates to their equilibrated levels. Since the standard version of CBM/OZIPM did not account for these two concentrations from aloft, we modified the inputs to the CBM/OZIPM model and introduced BZA and PAN as if they were part of the hydrocarbons found aloft for each day. Table 4-5 presents the results obtained when BZA and PAN are entrained in this manner. We see that the entrainment of BZA and PAN in the CBM/OZIPM model produces results that are in much closer agreement with those of the SAI trajectory model. For all CBM/OZIPM relative prediction calculations (discussed in section 5), we included entrainment of BZA and PAN. Our understanding of atmospheric chemistry indicates that some such intermediates must exist during the day, even though they may not be measured. Virtually any modern photochemical mechanism should respond in a fashion similar to that of the CBM used in this study, so the results are not considered to be specific to the CBM. Also, this addition to the CBM/OZIPM model is not considered to be an exercise in curve-fitting. One of the objectives of this project has been to determine the specific differing features of the models that explain significant differences in their results. This entrainment feature was added to the CBM/OZIPM to confirm our postulation that such a difference between the SAI trajectory model and the CBM/OZIPM would explain much of the differences in the result of the models.

A further comparison of concentration predictions between the SAI trajectory model and the CBM/OZIPM is shown in figure 4-1, which presents comparisons of NO_x, PAR, ETH, BZA, PAN, and ozone for 29 July 1977. As indicated in this table, species concentrations from both models are in close agreement. Additional comparisons of ozone concentrations predicted from the CBM/OZIPM calculations were made with data observed at monitoring stations along each trajectory. The results of these comparisons are shown in figure 4-2.

TABLE 4-4. ALOFT CONCENTRATIONS OF BZA AND PAN USED IN THE SAI TRAJECTORY MODEL AND THE CBM/OZIPM MODEL (ppm)

Date--1977	BZZ	PAN
21 July	0.001	0.001
29 July	0.0009	0.001
3 August	0.0011	0.0014
2 September	>0.00005	>0.00005

49r 81 9

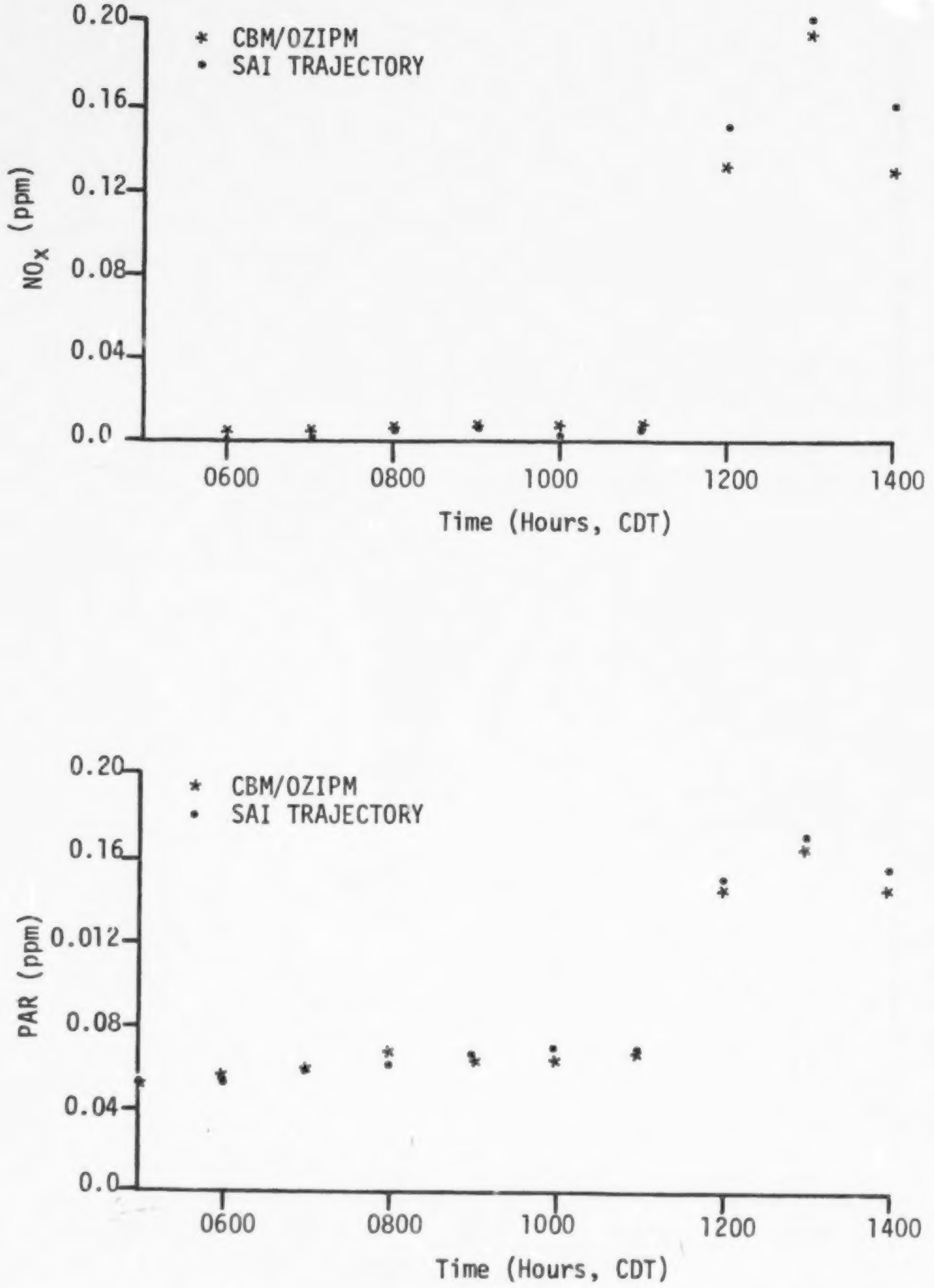
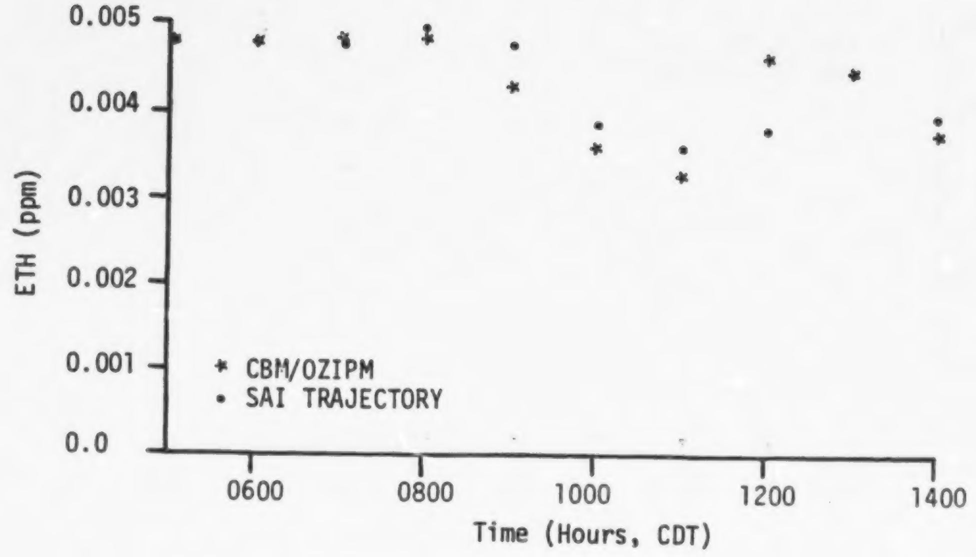


Figure 4-1. Comparison of NO$_x$, PAR, ETH, BZA, PAN, and ozone for the SAI trajectory and CBM/OZIPM models for 29 July 1977.



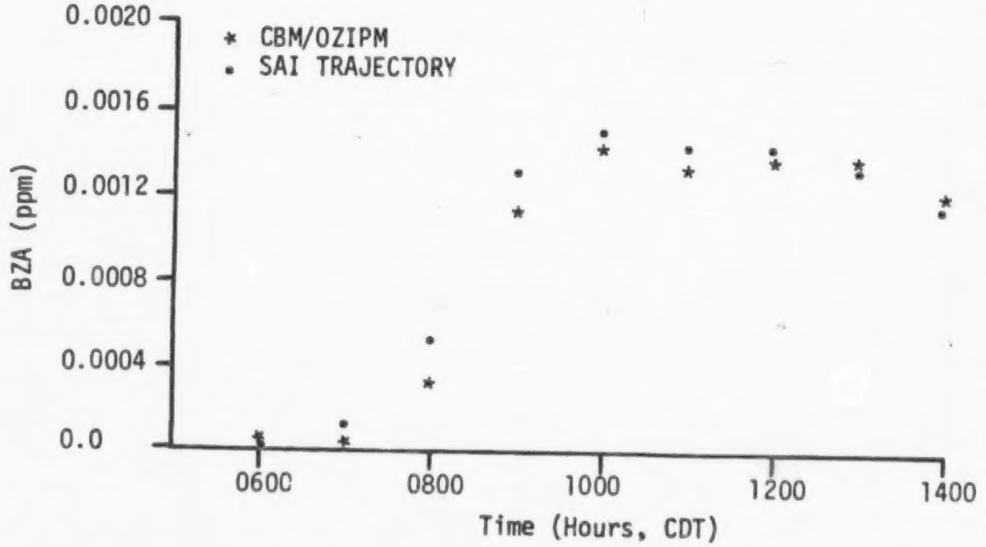
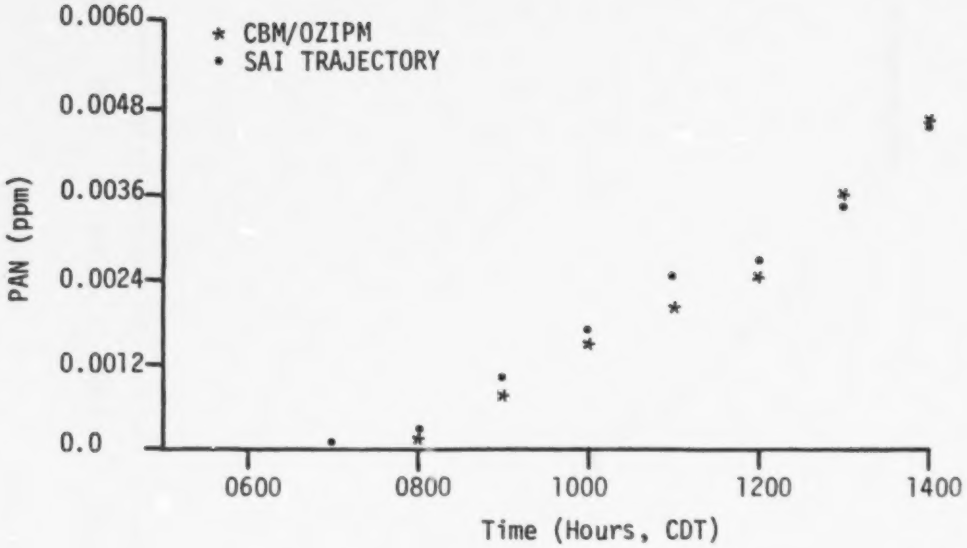


Figure 4-1 (continued)



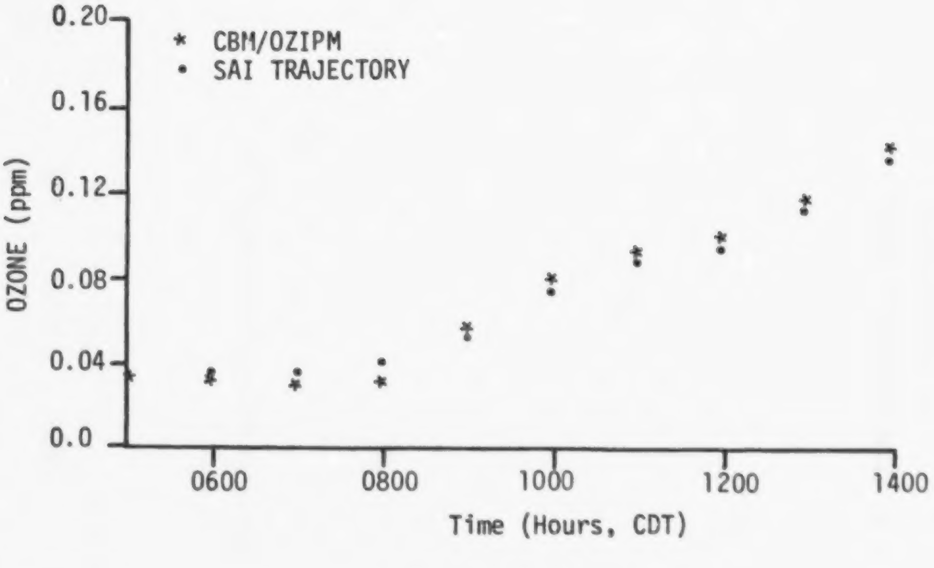
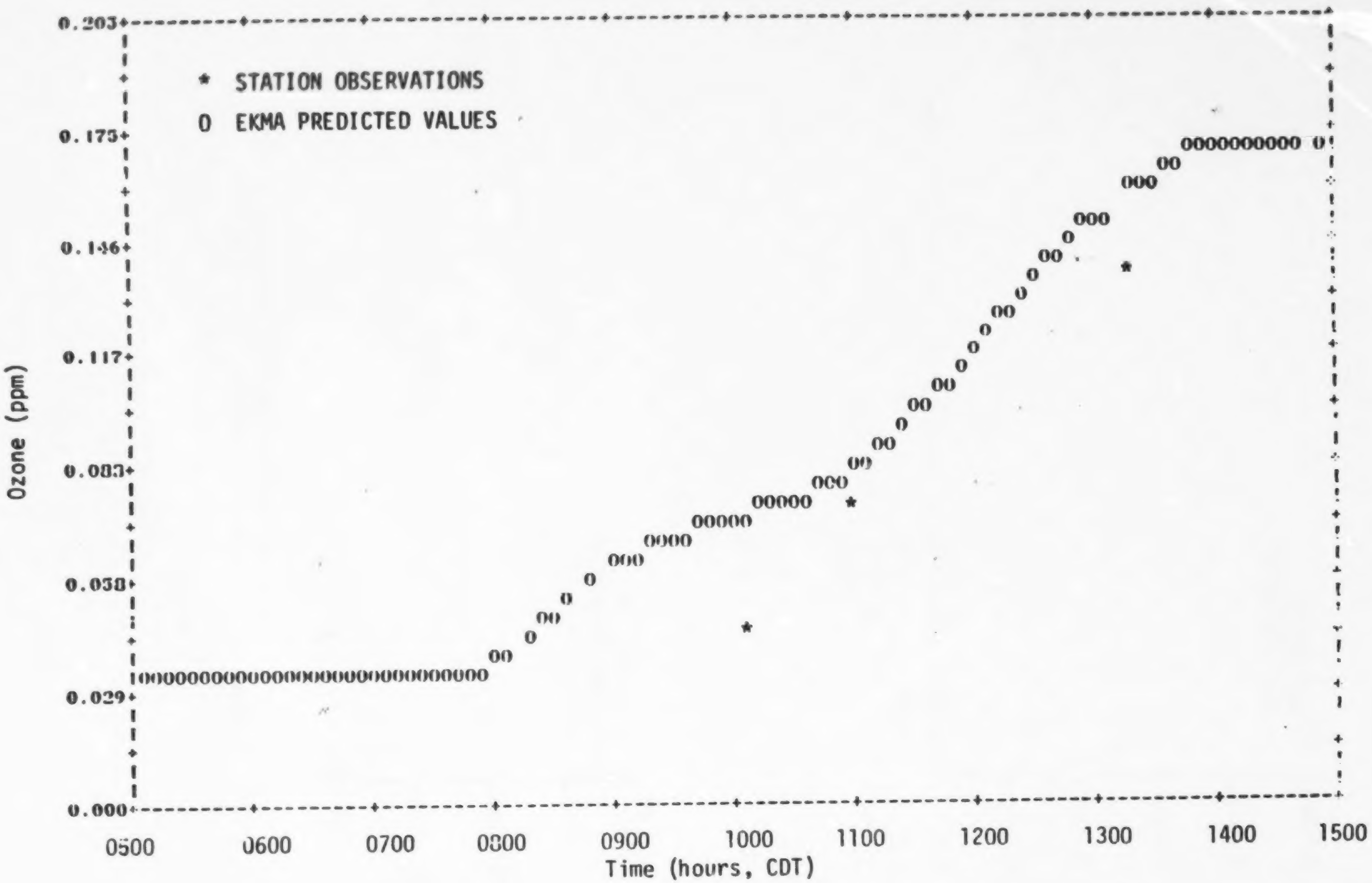
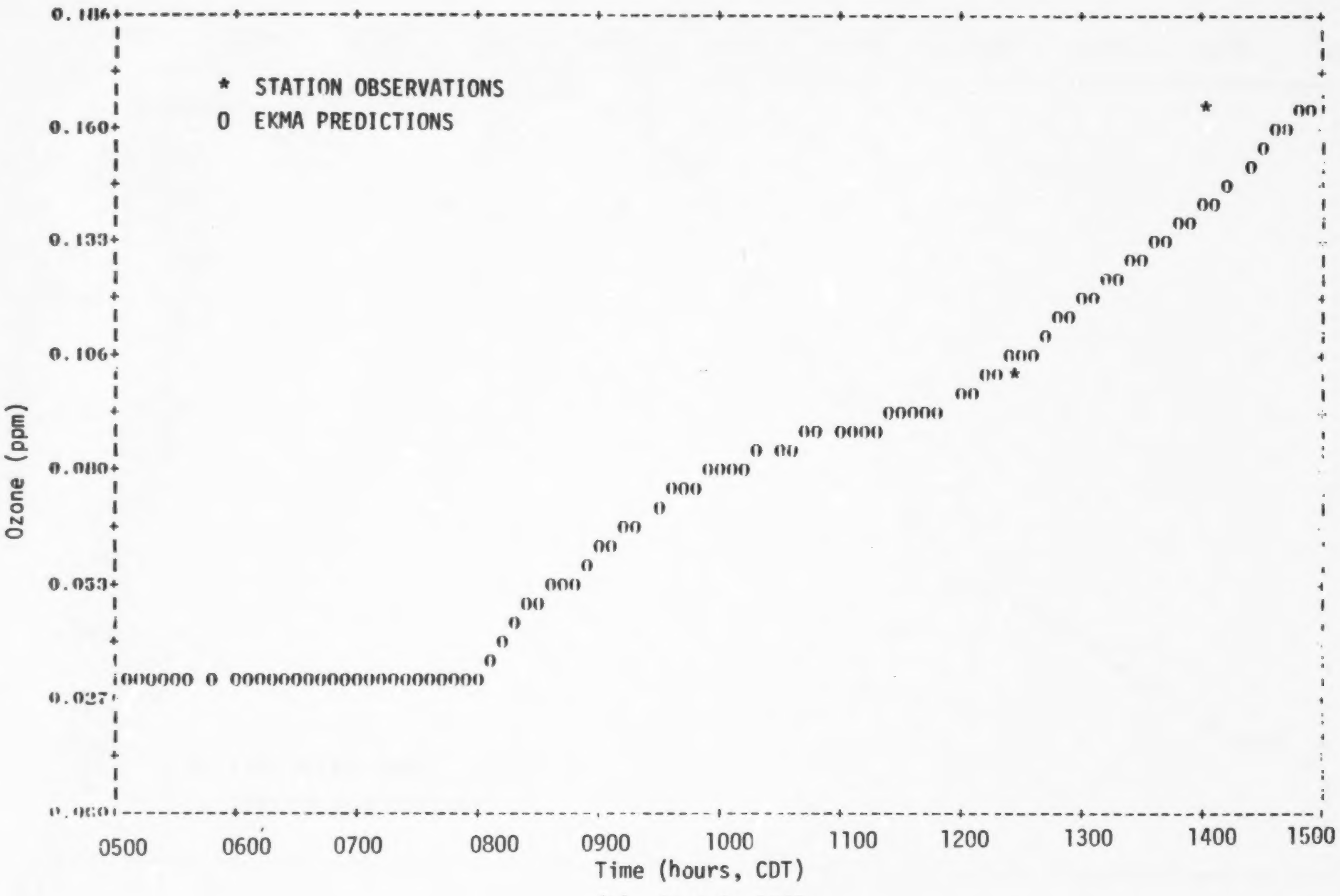


Figure 4-1 (concluded).



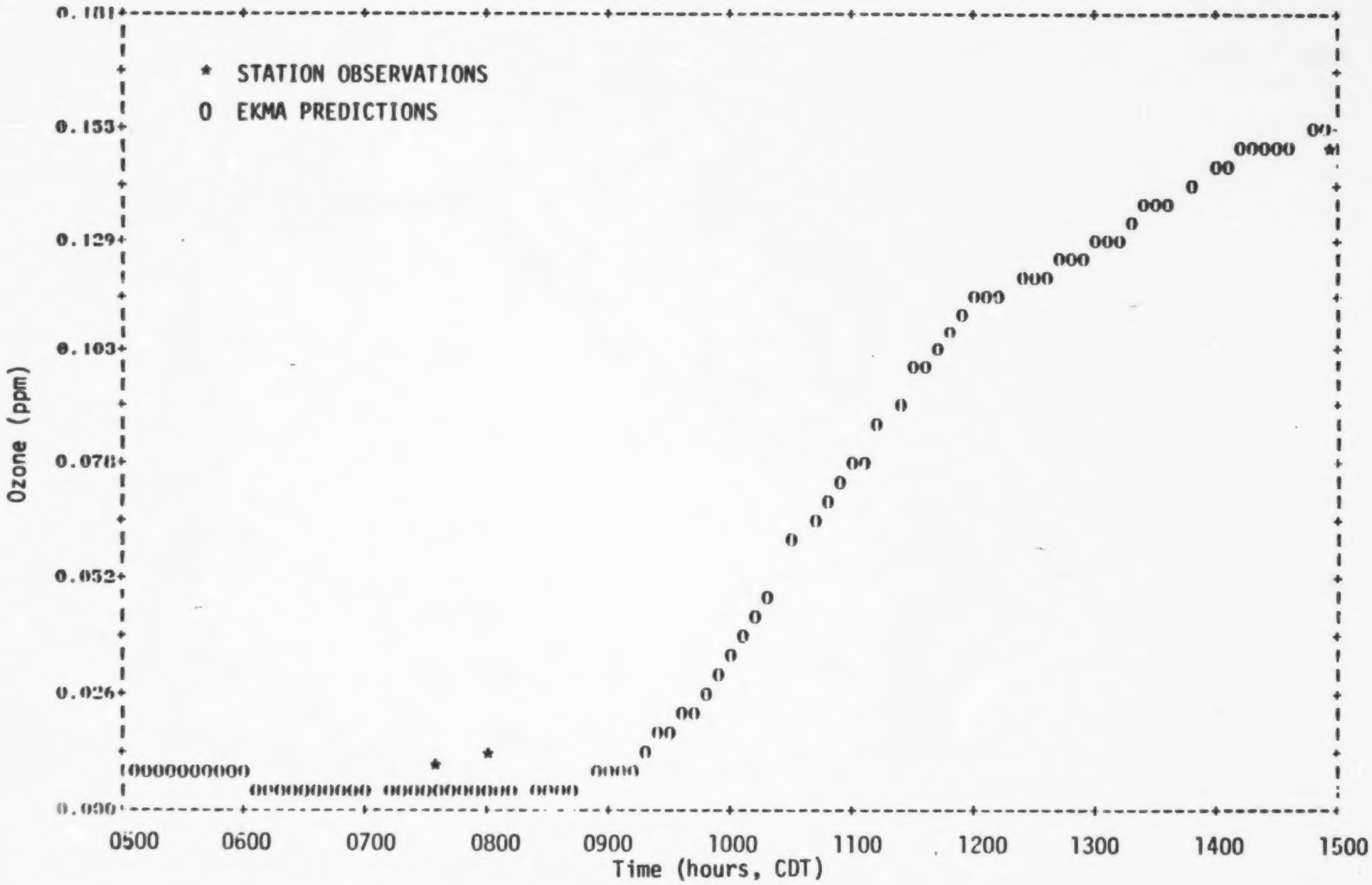
(a) 21 July 1977

Figure 4-2 Comparison between station-observed ozone and CBM/OZIPM predictions.



(b) 29 July 1977

Figure 4-2 (continued).



(c) 3 August 1977

Figure 4-2 (continued).

49r 81 18

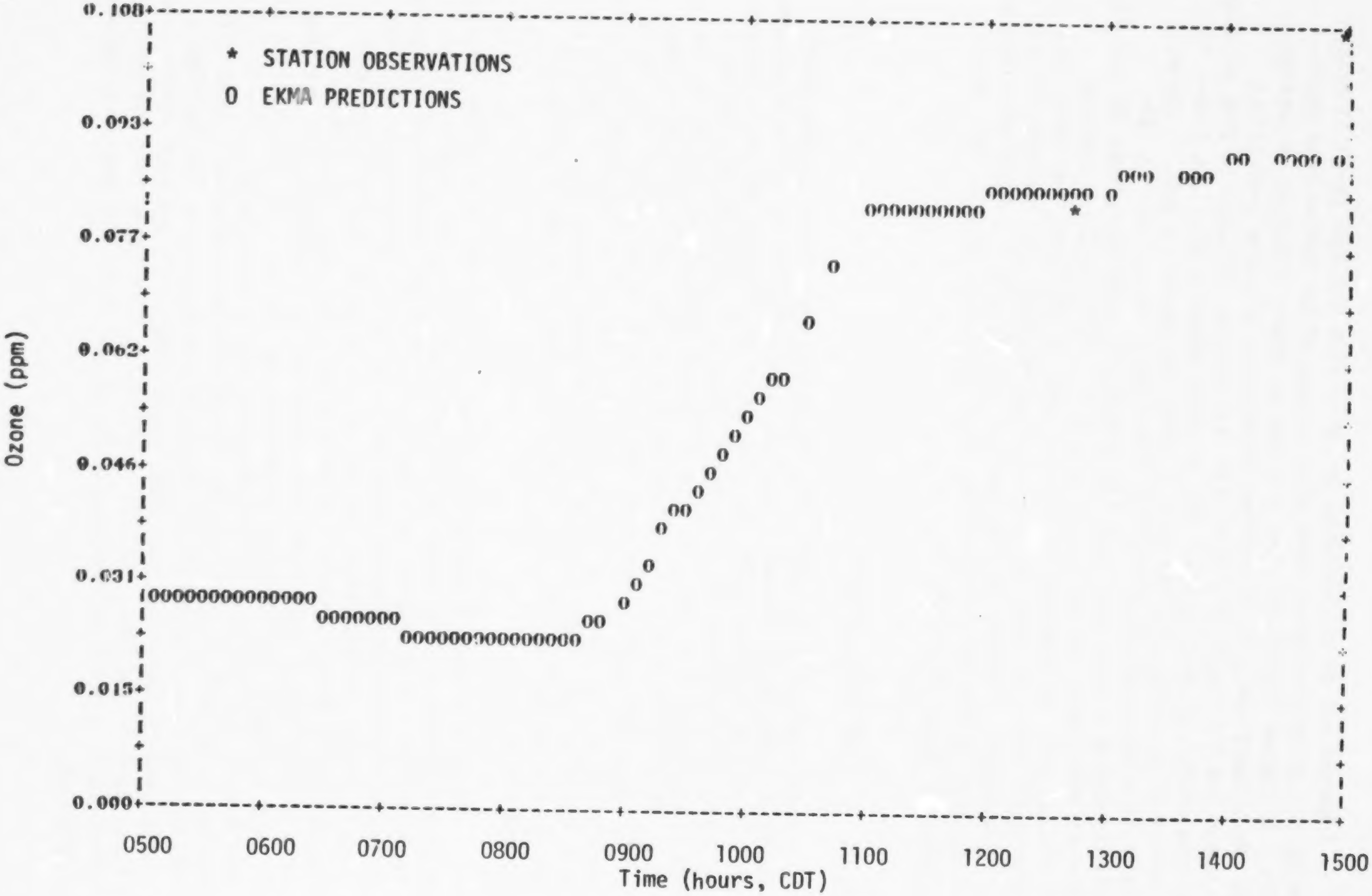


Figure 4-2 (concluded).

(d) 2 September 1977

A second set of calculations was made with the same Level II EKMA, using the propylene/butane chemistry instead of the Carbon-Bond chemistry. All other inputs remained the same as those discussed in section 3. No attempt was made to resolve differences in ozone predictions between the SAI trajectory model and this version of Level II EKMA because of the different chemistries. The absolute ozone predictions (shown in table 4-1) obtained with the propylene/butane chemistry are, in general, lower than those obtained from the CBM/OZIPM. These Level II EKMA predictions are also lower than the CBM/OZIPM predictions when BZA and PAN are not entrained (see tables 4-1 and 4-5). Investigative analysis indicates that one explanation of the lower predictions from this Level II EKMA model could be found in the outdated reaction rate constants in the propylene/butane mechanism (see section 6). Figure 4-3 shows the temporal ozone profile for the four modeling days along with observations made along the trajectory path.

LEVEL III EKMA MODEL RESULTS

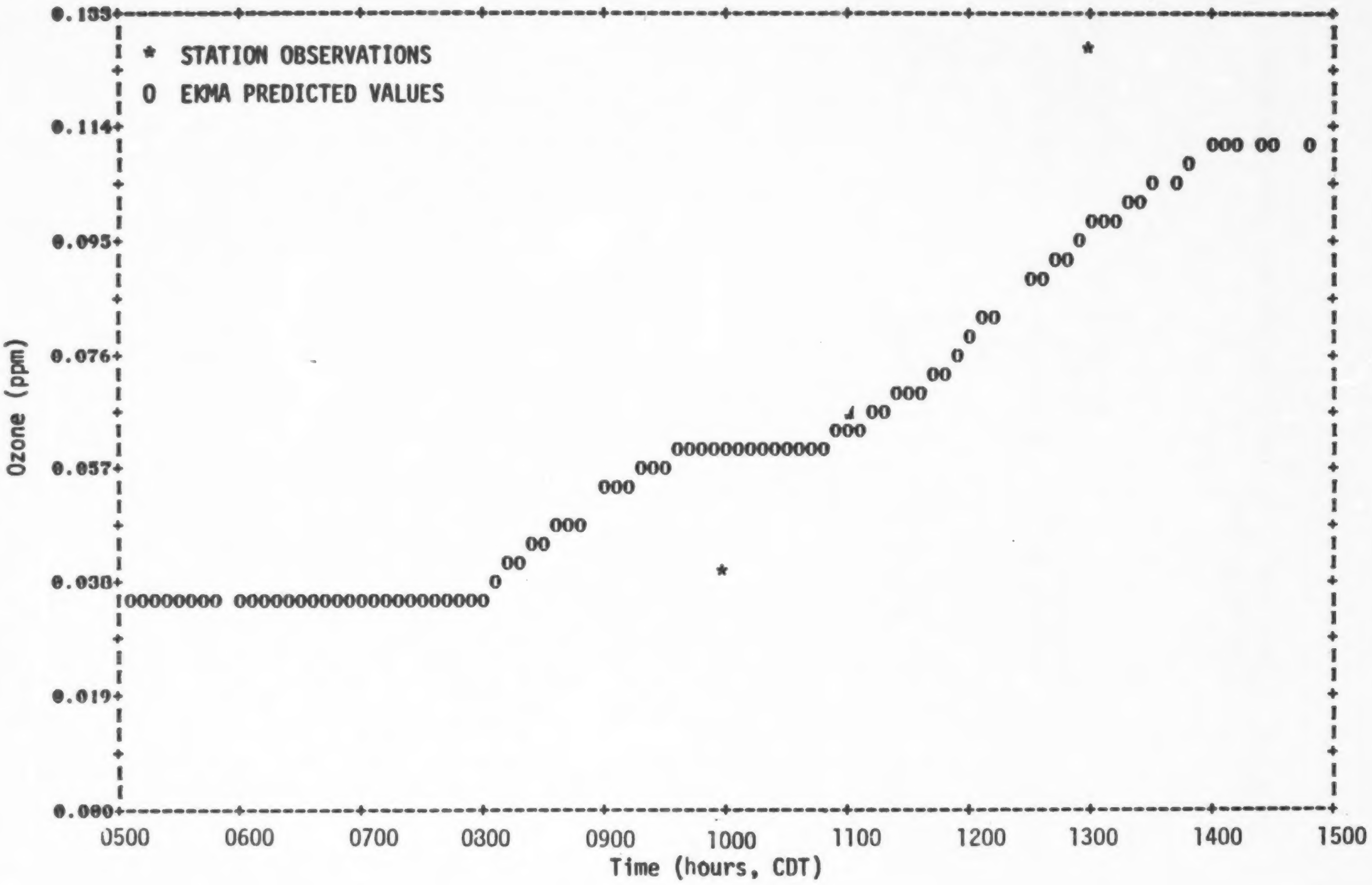
Since the Level III EKMA, SAI trajectory, and Level II EKMA model inputs are developed through different methodologies, we will not compare their absolute ozone predictions with those of previous models. Instead, we compare Level III EKMA ozone predictions with observations and with results obtained with the use of a different chemical mechanism in the Level III EKMA models. As seen in table 4-1, the Level III EKMA ozone predictions tend to be lower than the observed maximum ozone for all of the four modeling days. Note that the city-specific EKMA predictions are also usually lower than those of preceding model predictions. This result may be due in part to the conservative assumptions made in estimating NMOC levels aloft.

Figure 4-4 shows the ozone temporal profiles for each of the modeling days along with station observations obtained along the straight-line trajectories. A second set of Level III EKMA model calculations obtained using the Carbon-Bond chemistry shows results similar to those obtained with the Level II EKMA calculations using Carbon-Bond chemistry (when compared with observations). In most cases, the Level III EKMA/CBM predictions tend to be higher than those of the standard Level III EKMA. Figure 4-5 shows the temporal ozone profiles for each of the modeling days along with station observations obtained along the straight-line trajectories. Analysis of the detailed computer calculations shows that the results can be explained by the aldehyde concentrations and photolysis rates used in the propylene/butane mechanism, which are much higher than those used in the CBM. The CBM reactivities were taken from the Level II EKMA study, whereas default reactivity was used for the propylene/butane mechanism.

TABLE 4-5. COMPARISON OF SAI TRAJECTORY AND THE CBM/OZIPM MODEL OZONE PREDICTIONS

(ppm)

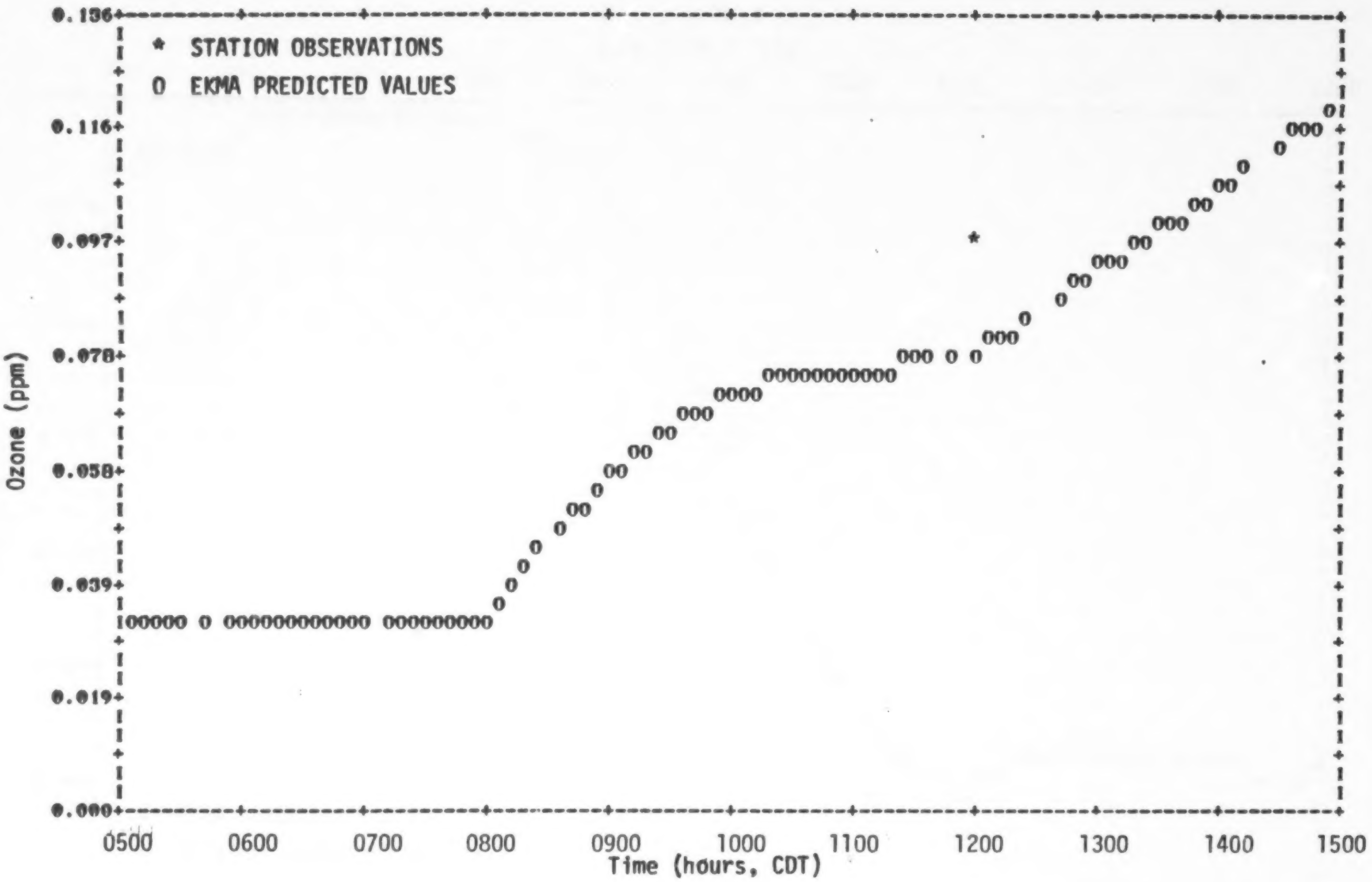
Date--1977	Predicted O_3 (SAI Trajectory)	Predicted O_3 (CBM/OZIPM) w/o BZA and PAN)	Predicted O_3 (CBM/OZIPM) with BZA and PAN)
21 July	0.154	0.138	0.154
29 July	0.138	0.125	0.140
3 August	0.150	0.138	0.150
2 September	0.091	0.091	0.091



(a) 21 July 1977

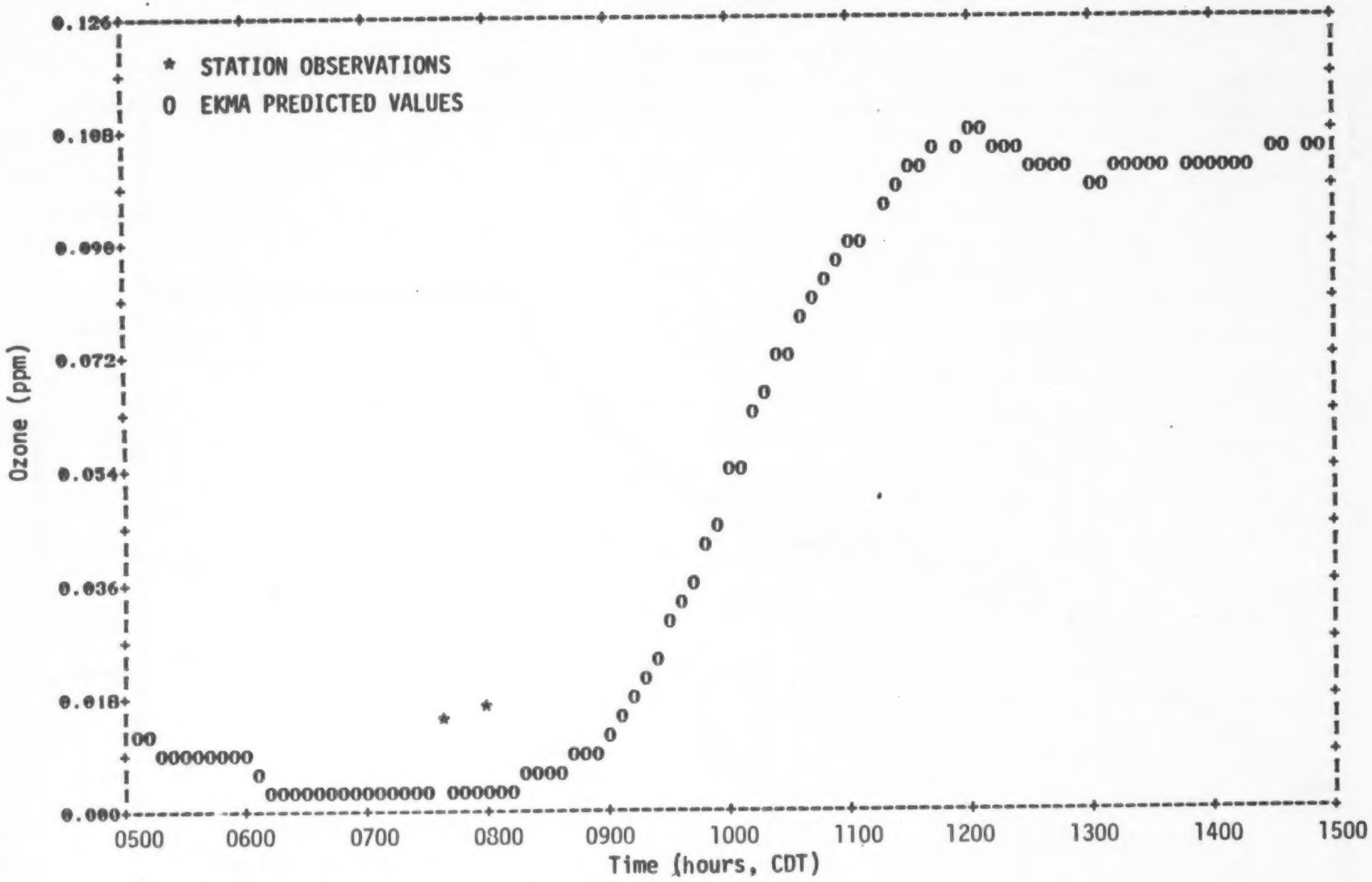
Figure 4-3. Level II EKMA trajectory for Tulsa, Oklahoma.

49r 81 18



(b) 29 July 1977

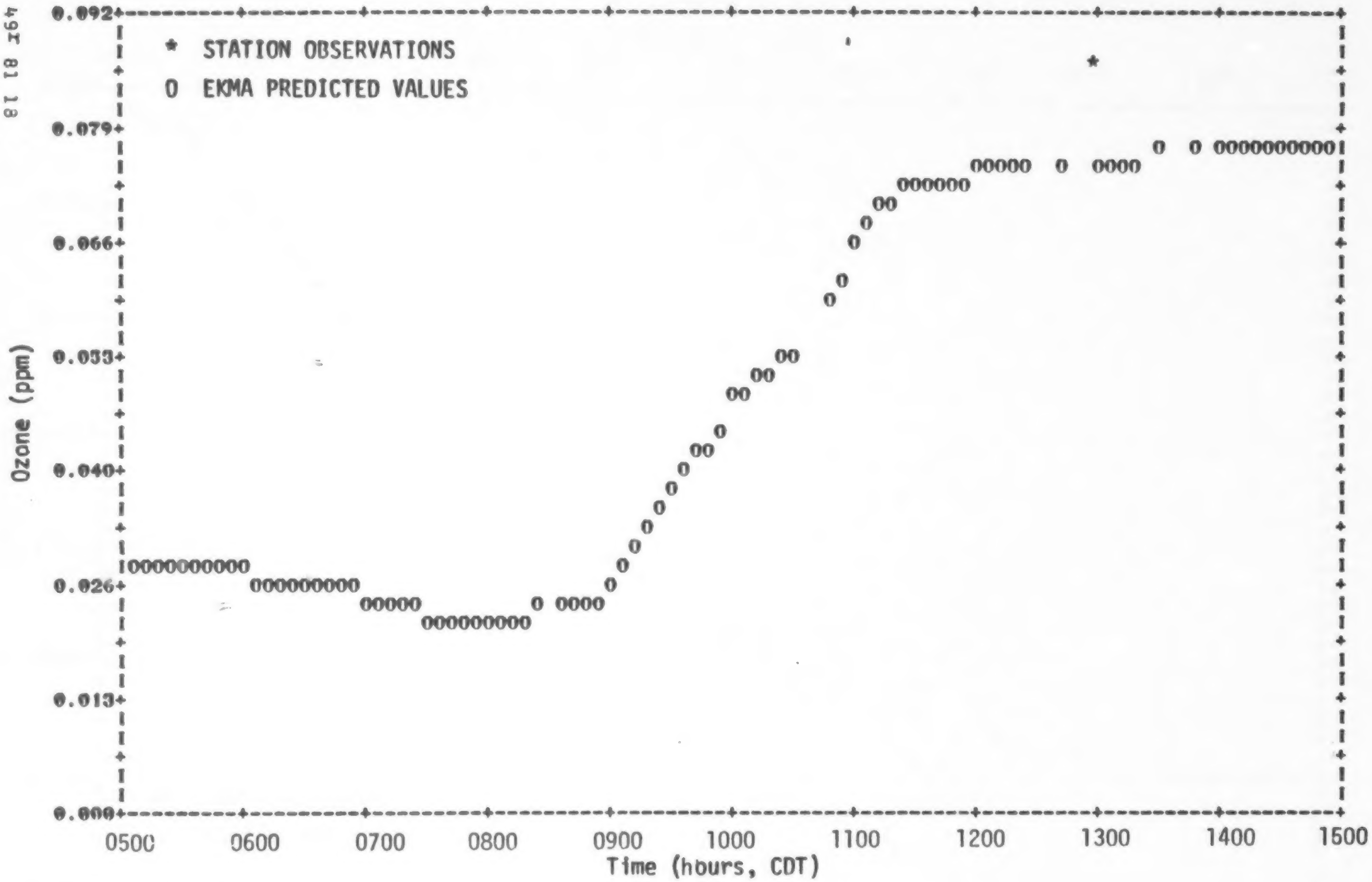
Figure 4-3 (Continued).



(c) 3 August 1977

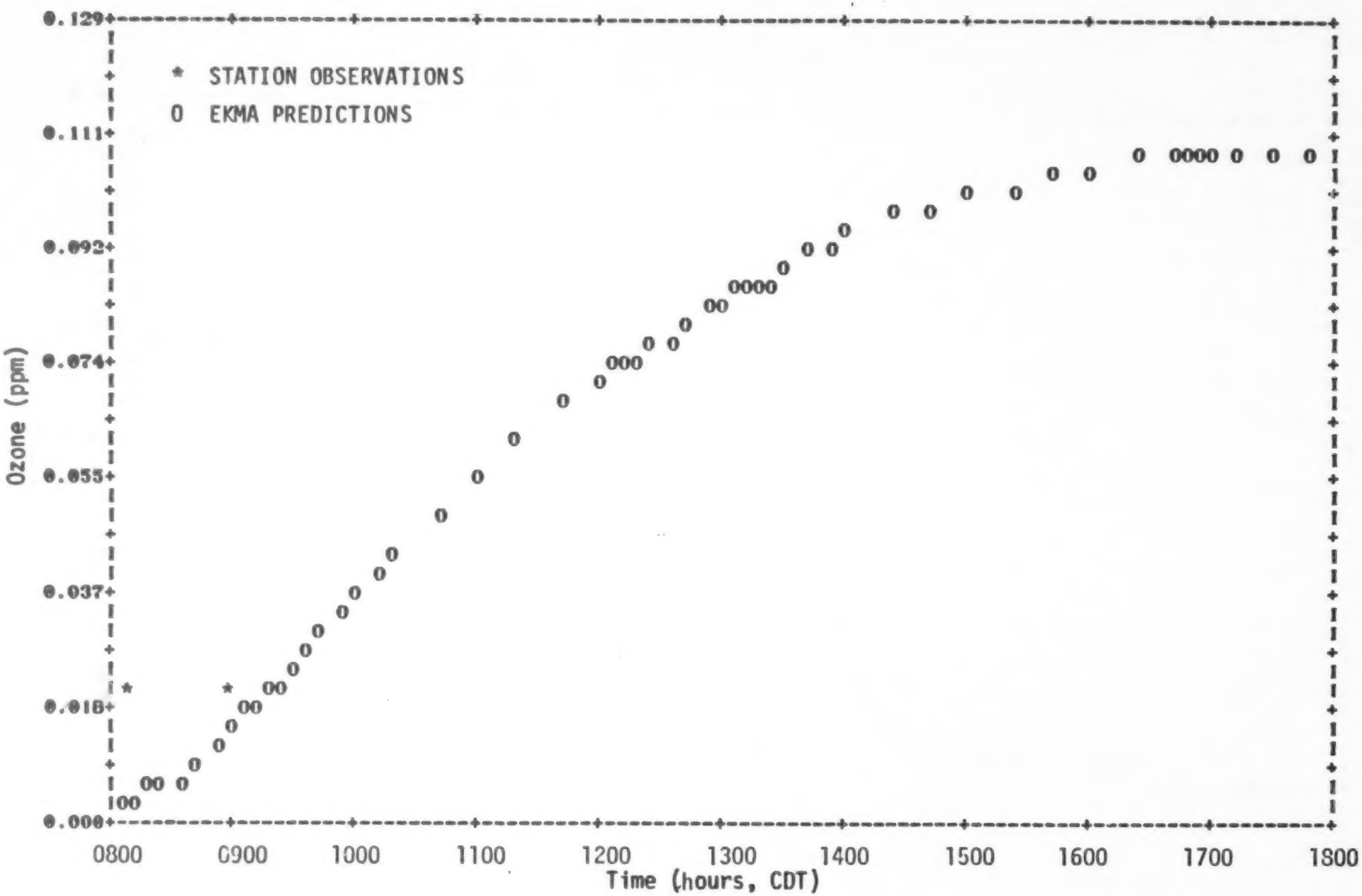
Figure 4-3 (Continued).

49r 81 18



(d) 2 September 1977

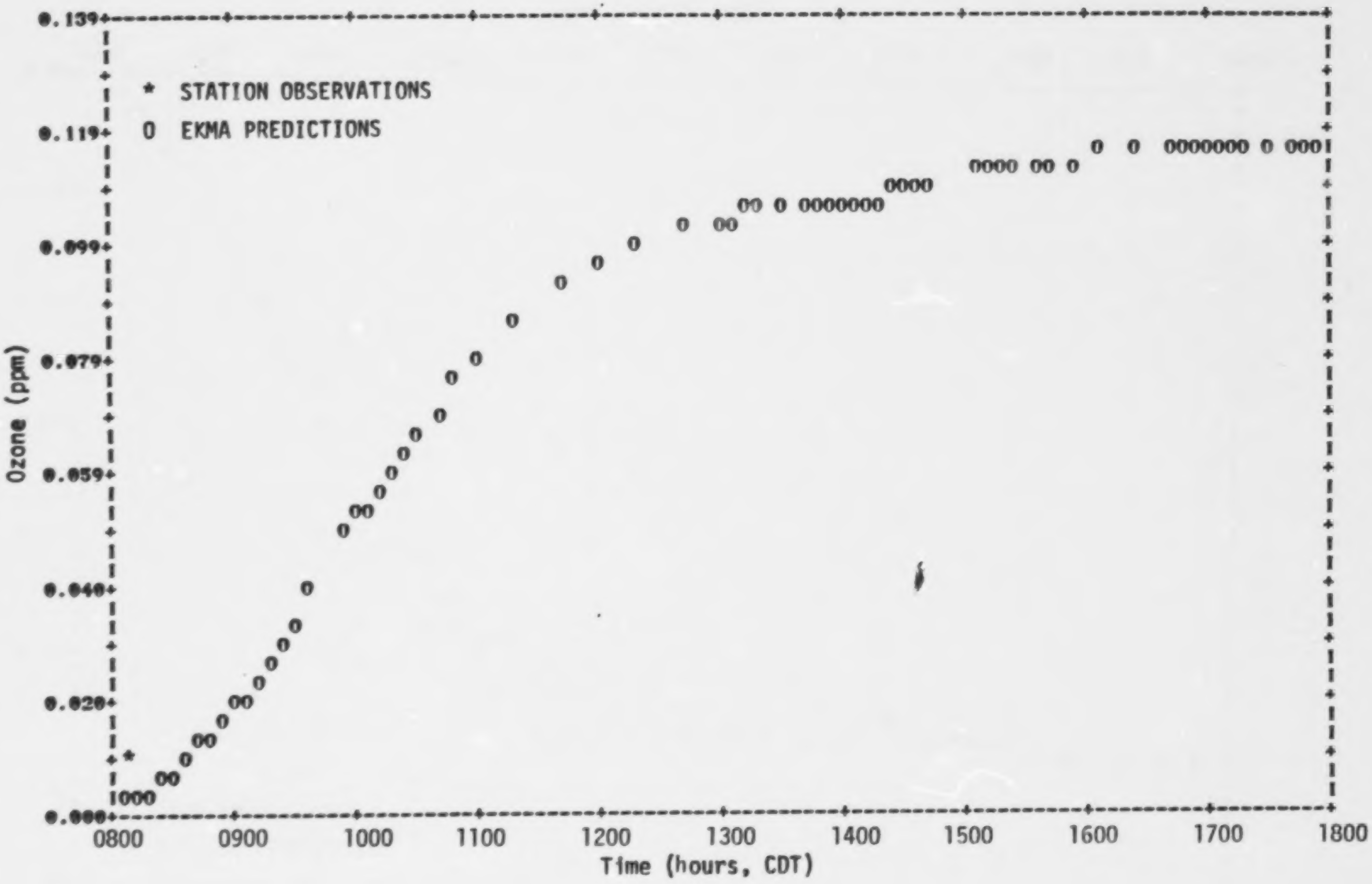
Figure 4-3 (Concluded).



(a) 21 July 1977

Figure 4-4. Level III EKMA trajectory for Tulsa, Oklahoma.

49r 81 18



(b) 29 July 1977

Figure 4-4 (Continued).

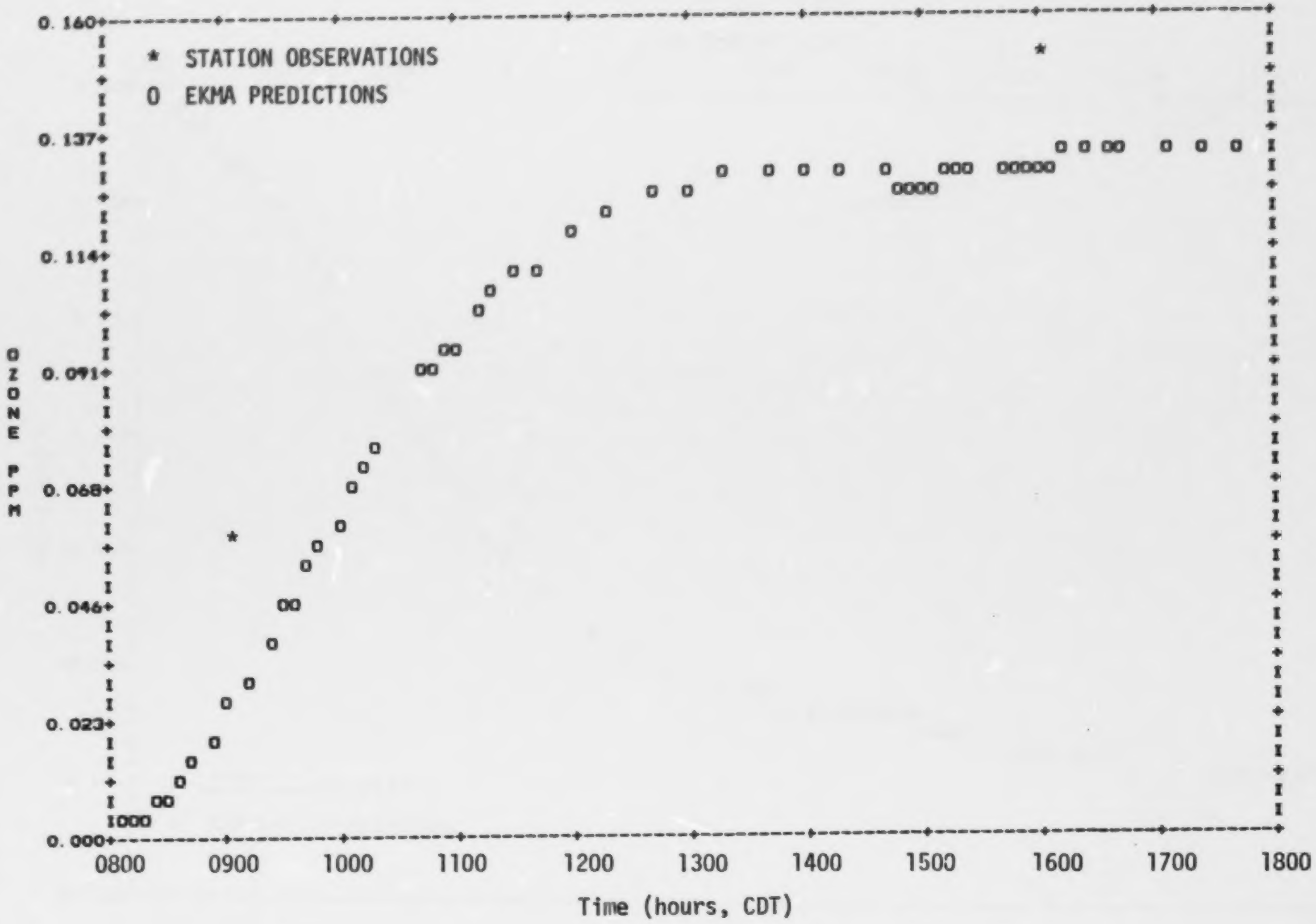
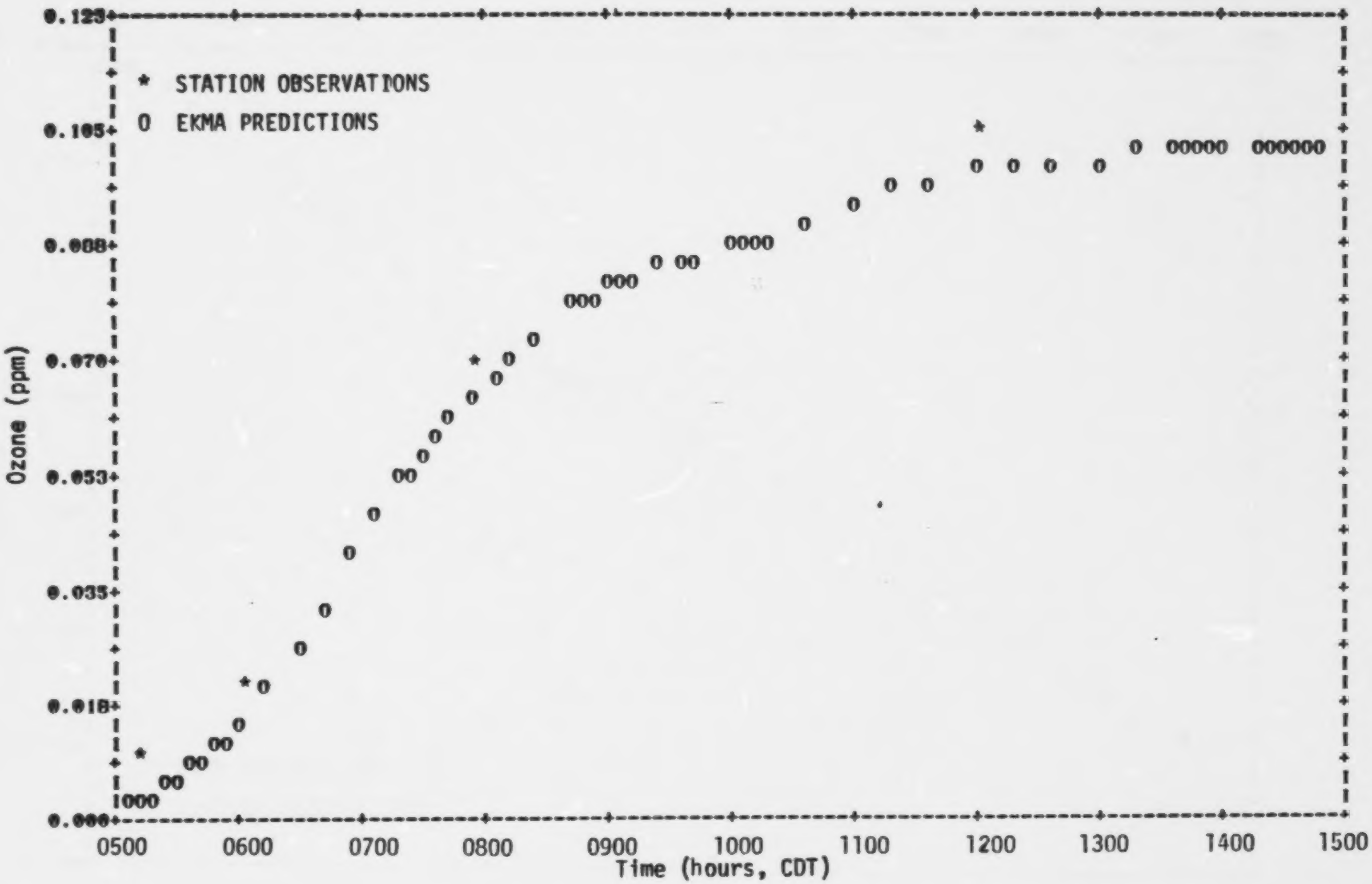
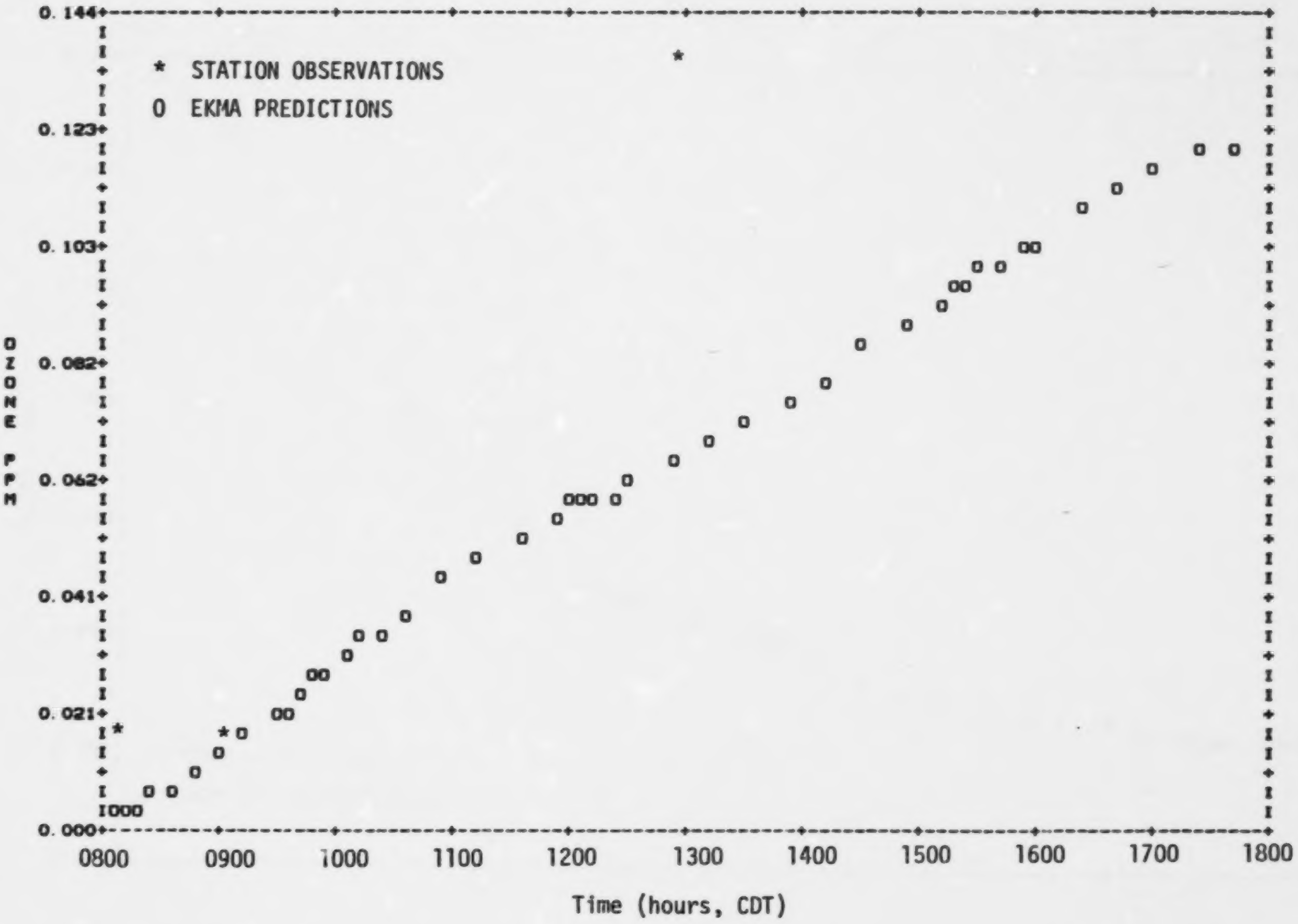


Figure 4-4 (Continued). (c) 3 August 1977



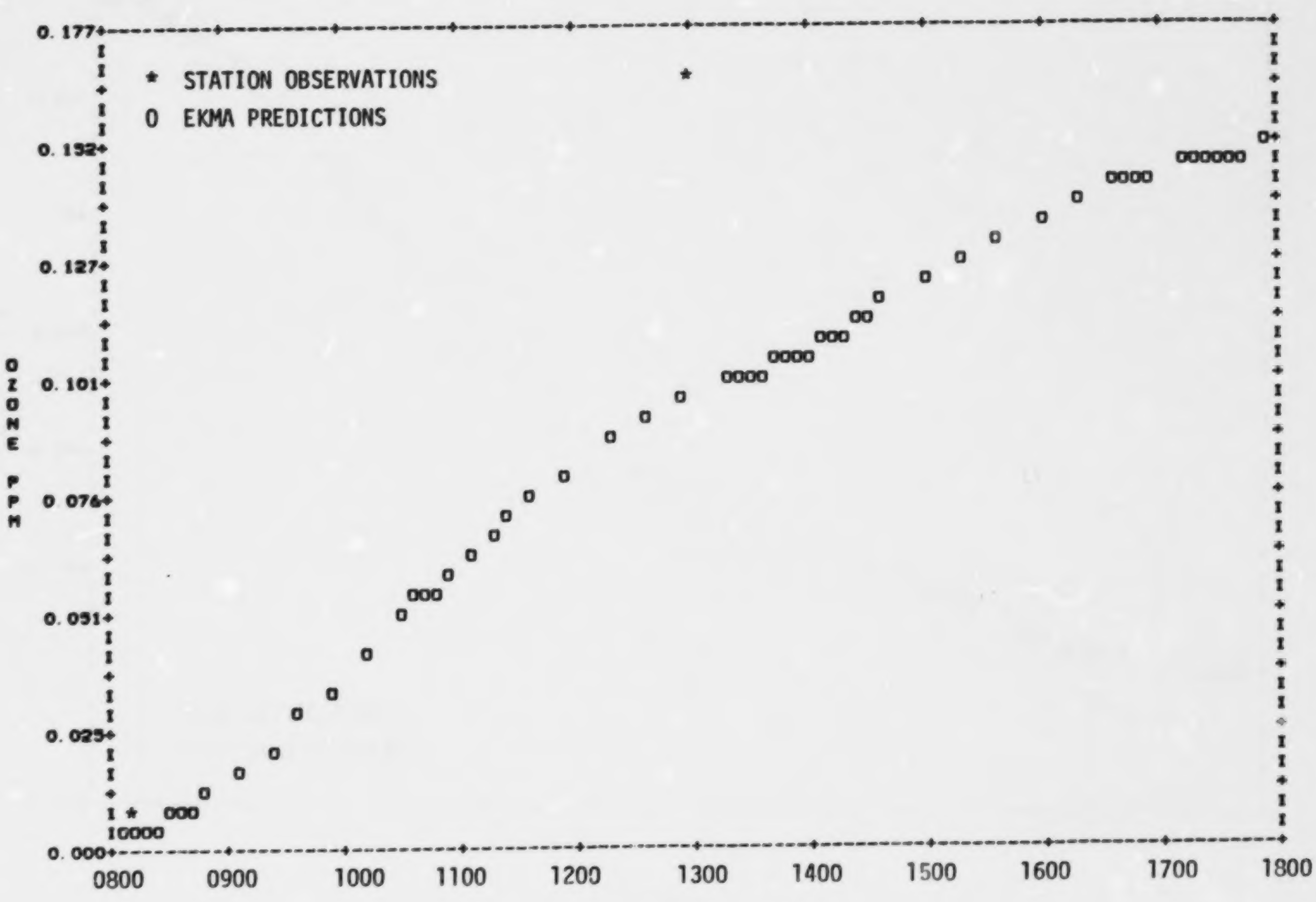
(d) 2 September 1977

Figure 4-4 (Concluded).



(a) 21 July 1977

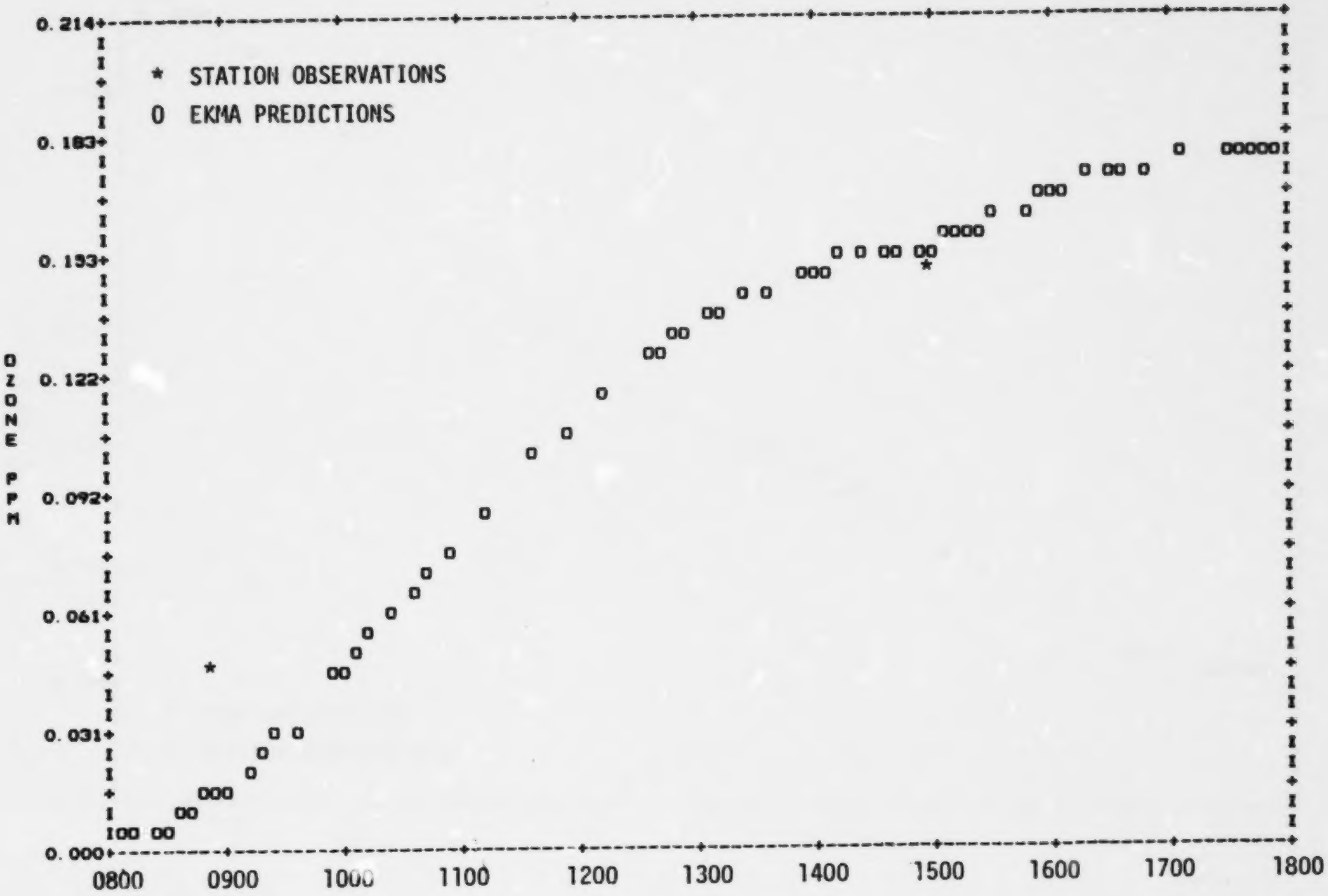
Figure 4-5. Level III EKMA trajectory for Tulsa, Oklahoma using the Carbon-Bond Mechanism.



(b) 29 July 1977

Figure 4-5 (Continued).

49r 81 18

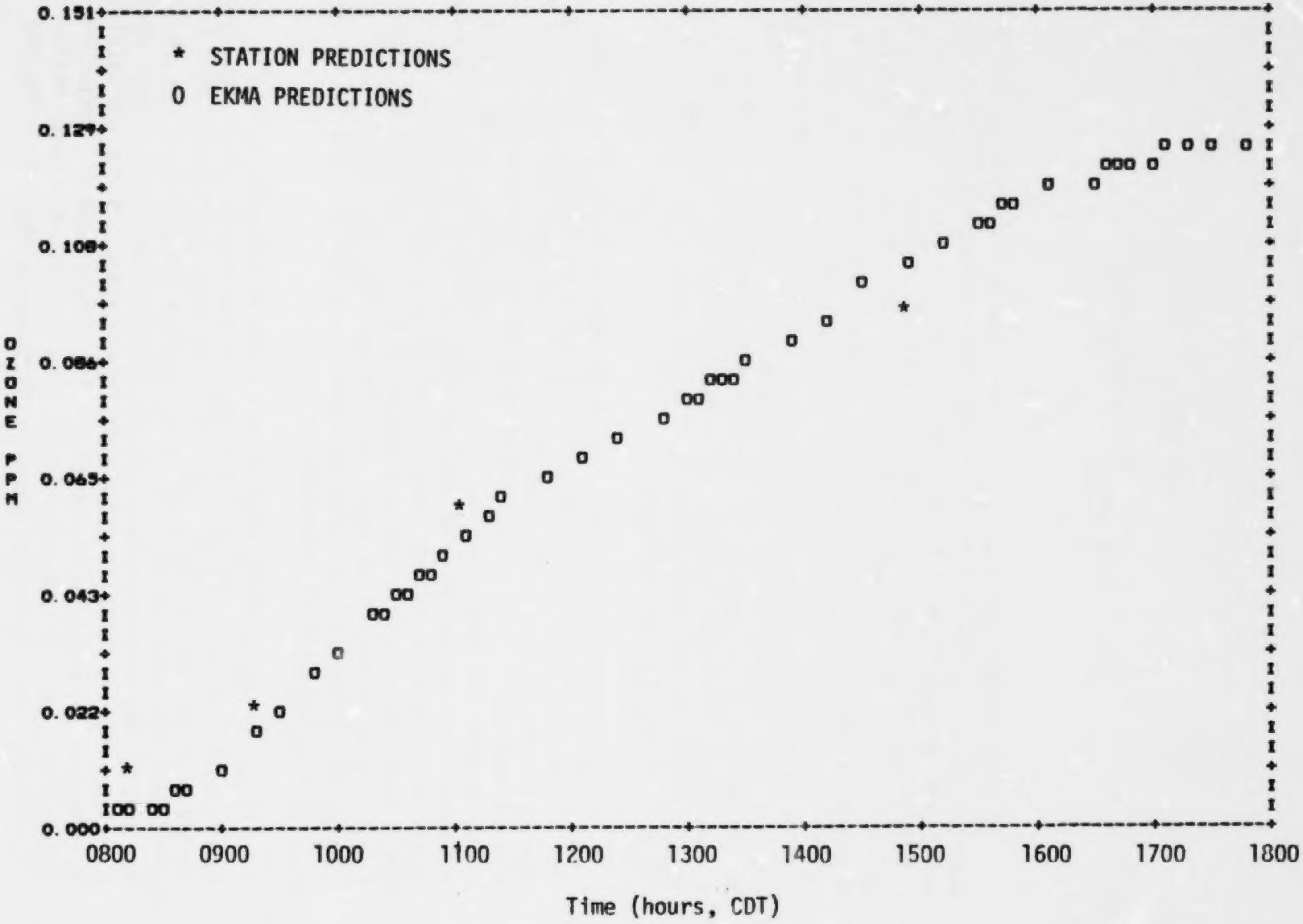


Time (hours, CDT)

(c) 3 August 1977

Figure 4-5 (Continued).

49r 81 18



(d) 2 September 1977

Figure 4-5 (Concluded).

SECTION 5

EKMA ISOPLETH CALCULATIONS

In this section, we discuss the use of the EKMA models to estimate the results of control scenarios designed to produce ozone reductions sufficient to meet federal or state standards. Predictions obtained using ~~the~~ EKMA isopleth diagrams are compared with the predictions obtained from the SAI Airshed Model. Unfortunately, at the time of this writing, only one modeling day (29 July 1977) in the Airshed modeling effort had been investigated using a 1987 emissions inventory. Thus, we can compare only results of the SAI Airshed and EKMA models for the 29 July 1977 modeling day. We also present Level III EKMA predictions for 21 July 1977 and 3 August 1977 so that they can be compared with Airshed Model results at a future date. No effort is made to compare EKMA predictions for 2 September 1977 since the maximum observed ozone on that day was less than the federal standard of 0.12 ppm.

Emission inventory summaries are presented in table 5-1. These inventories were developed by Engineering Science (1979) for the modeling year 1977 and for two future-year scenarios (1982 and 1987). Current SAI Airshed modeling efforts have concentrated on the 1987 predictions. Table 5-1 indicates that Reactive VOC is reduced 31.5 percent and NO_x is reduced 3.7 percent in the period from 1977 to 1987. Additional control measures, which should lead to greater ozone reductions, are presented in table 5-2. These additional measures would produce a 47.5 percent VOC reduction in the period from 1977 to 1987. SAI Airshed modeling efforts to date have performed simulations using options I, II, and V (table 5-2) with 29 July 1977 meteorological conditions.

In all of the original 1987 Airshed simulations, the initial, boundary, and aloft conditions were kept at the same values as those used in the 1977 validation runs. The reason for this is that the 1977 initial conditions were considered to be at background concentrations (0.20 ppmC for NMHC). Any concentrations greater than the background values would have been changed to reflect the emissions changes. Since the Level II EKMA models use the same inputs as the SAI Airshed and SAI trajectory models, the Level II EKMA models were also run with constant initial conditions. Table 5-3 shows ozone predictions obtained from the SAI

TABLE 5-1. EMISSION INVENTORY SUMMARY FOR THE TULSA STUDY AREA

Year	Source	Emissions tons/day Reactive VOC (ppmC)	NO$_x$[*] (ppm)
1977	Point	104.4	126.0
	Area[†]	29.3	24.9
	Line	65.4	58.3
	Total	199.1	209.2
1982	Point	62.7	124.8
	Area[†]	39.1	29.2
	Line	44.3	49.6
	Total	146.1	203.6
1987	Point	66.3	127.3
	Area[†]	41.9	33.7
	Line	28.2	40.3
	Total	136.4	201.3

---

[*] NO$_x$ as NO$_2$.

[†] Not including mobile sources.

49r 81 13

TABLE 5-2. CONTROL STRATEGIES TO BE USED IN THE TULSA MODELING STUDY

	1977 (tons/day)	1987 (tons/day)	Percentage Reduction
Option I Present strategy as presented by the state of Oklahoma	199.1	136.4	31.5%
Option II Option I Vehicle inspection and maintenance (VIM)	N/A	130.9	34.3
Option III Option II Oil/water separators Fiberglass products	N/A	117.7	40.9
Option IV Option III Stage I vapor recovery	N/A	112.1	43.7
Option V Option IV Rideshire, park and ride Fleet conversion	N/A	110.3	44.6
Option VI Option V Stage II vapor recovery Transit improvements Bicycle paths Traffic flow improvements	N/A	104.4	47.5

N/A = Not applicable.

TABLE 5-3. OZONE PREDICTIONS FROM EKMA MODEL SINGLE-DAY DIAGRAMS
(ppm)

Date	SAI Airshed Model Results	Percentage* Change in O_3	Level III EKMA Model Results	Percentage* Change in O_3	Level III EKMA with CBM Model Results	Percentage* Change in O_3
29 July 1977	0.17	--	--	--	--	--
29 July 1987--option I	0.14	17.6%	0.145	14.7%	0.12	29.4%
29 July 1987--option II	0.138	18.8	0.14	17.6	0.11	35.3
29 July 1987--option III	0.131	22.9	0.125	26.4	0.095	44.1
(observed O_3 = 0.19						
21 July 1977	0.14	--	--	--	--	--
21 July 1987--option I[†]	--	--	0.11	21.4	0.08	42.9
21 July 1987--option II[†]	--	--	0.105	25.0	0.075	46.4
21 July 1987--option V[†]	--	--	0.09	35.7	0.05	64.2
(observed O_3 = 0.14 ppm)						
3 August 1977	0.12	--	--	--	--	--
3 August 1987--option I[†]	--	--	0.132	12.0	0.12	20.0
3 August 1987--option II[†]	--	--	0.13	13.3	0.115	23.3
3 August 1987--option V[†]	--	--	0.12	20.0	0.10	33.3
(observed O_3 = 0.15 ppm)						

---

[*] Percentage change in ozone = $\dfrac{(\text{Observed } O_3) - (\text{Predicted } O_3)}{(\text{Observed } O_3)} \times 100.$

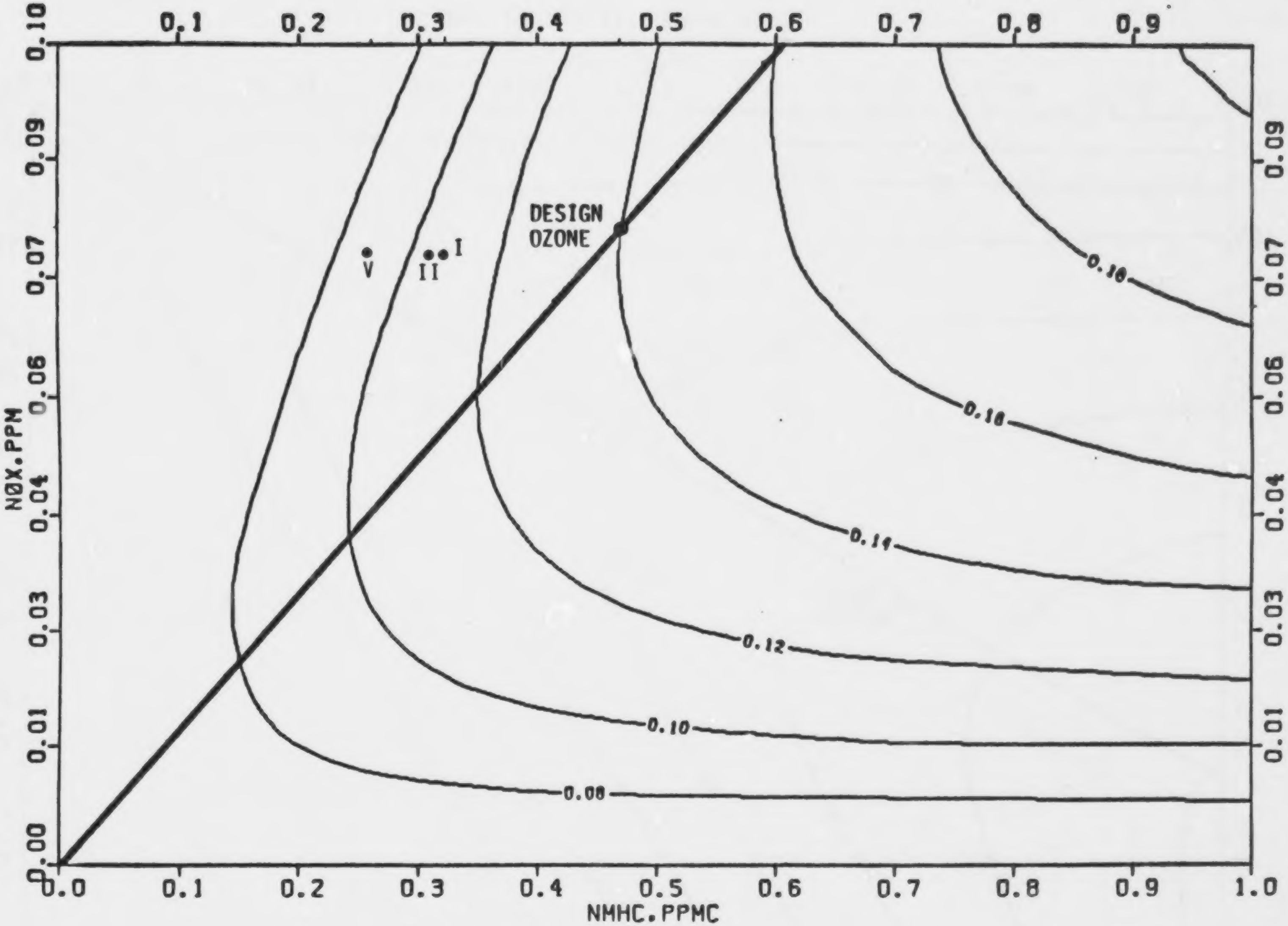
[†] Airshed simulations for these days had not been performed at the time of the writing of this document.

Airshed Model using the control options I, II, and V (table 5-2). For the Level III EKMA simulations, we generated an isopleth for the base year using initial conditions described in section 3. Although the initial precursor conditions remained the same for 1977 and the future year (1987) in the Airshed Model simulations, the ozone value aloft was lowered from 0.08 ppm to 0.06 ppm in the future-year Level III EKMA simulations. A future-year isopleth with a lowered value of ozone aloft was generated by following the recommended procedures outlined in the Level III guidelines (EPA, 1980). The ozone value aloft was lowered by 0.01 ppm in the future year diagrams for all of the modeling days. Figures 5-1(a), (b), and (c) show the base case ozone isopleth diagrams for 21 July 1977, 29 July 1977, and 3 August 1977, respectively. Figures 5-1(d), (e), and (f) show the future-year diagrams for the same three days. A second set of base case and future year isopleths was generated for the three modeling days using the Carbon-Bond chemistry. These diagrams are shown in figure 5-2.

We compared current Airshed Model predictions with Level III EKMA predictions using emission reduction options I, II, and V on 29 July, 21 July, and 3 August. For these comparisons we used the base case diagrams [figures 5-1 (a) through (c) and figures 5-2 (a) through (c)] developed for the Level III EKMA and the Level III EKMA using the CBM. By using the base case diagram we can directly compare EKMA predictions with the airshed predictions since the ozone concentrations aloft were kept constant in the base case EKMA diagrams. Results of these comparisons are shown in table 5-3. From table 5-3 we see that the percentage change in ozone between the Level III EKMA using propylene/butane chemistry is similar to that in the airshed results, whereas the percentage change in ozone from the Level III EKMA using the CBM shows a greater sensitivity to the same emission reductions.

We also compared currrent Airshed Model predictions with Level III EKMA predictions using emission reduction options I, II, and V (table 5-2) in the future-year diagrams of 29 July, 21 July, and 3 August [figure 5-1 (d) (e), and (f) for the EKMA with propylene/butane chemistry and figure 5-2 (d),(e), and (f) for the EKMA using Carbon-Bond chemistry]. Results of this exercise are shown in table 5-4, which indicates that with similar reductions in hydrocarbon and NO_x the Level III EKMA models (both propylene/butane and CBM chemistry) produce ozone predictions lower than those of the SAI Airshed Model. Results obtained with the Level III EKMA model using the Carbon-Bond chemistry demonstrate the largest change in ozone level from these scenarios.

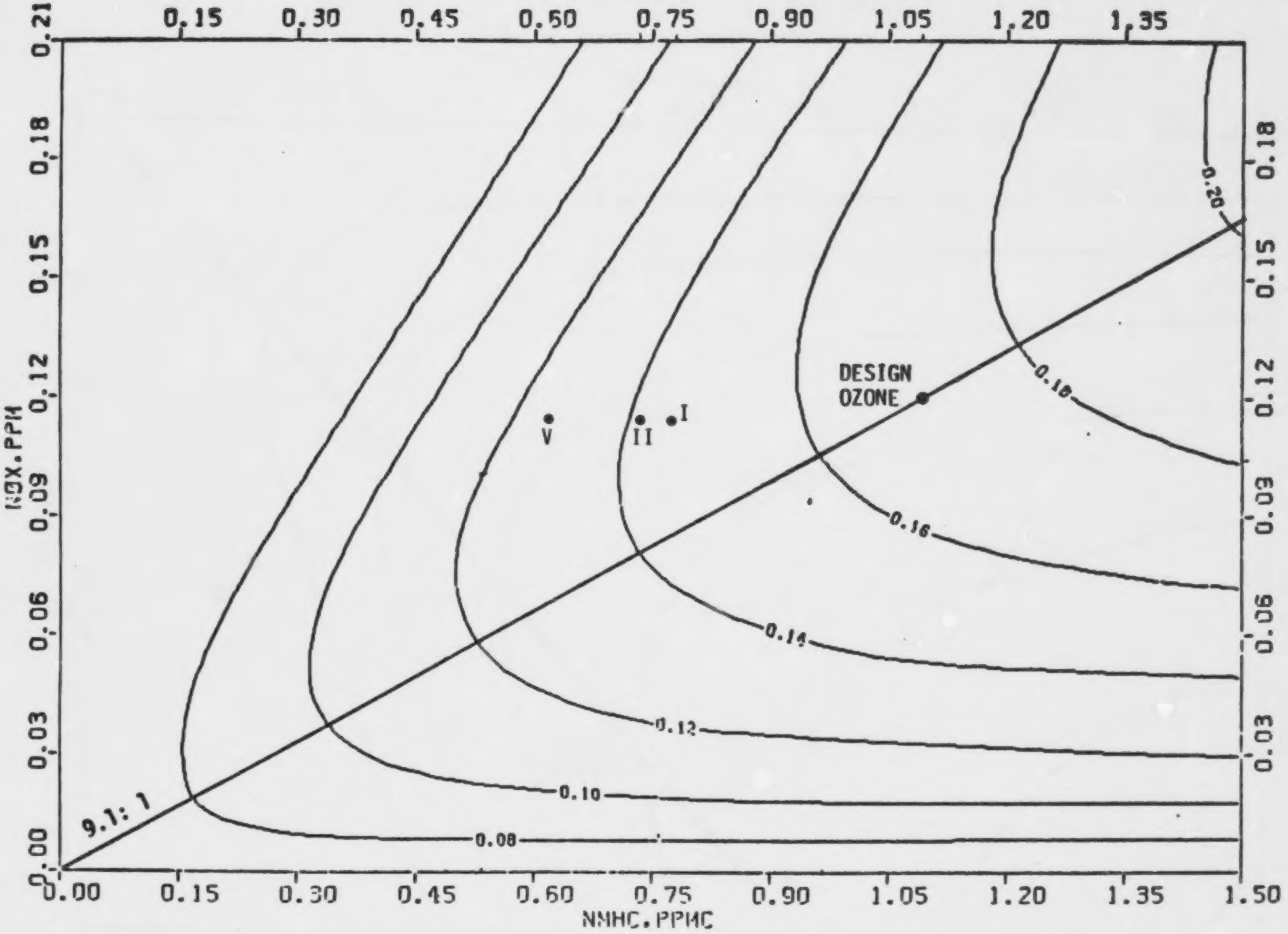
Following the Level III EKMA guidelines (October 1980, draft), we estimated the hydrocarbon reductions needed to comply with the federal ozone standard of 0.12 ppm. The results of this exercise are presented in table 5-5. As seen from this table, the standard Level III EKMA required



(a) 21 July 1977 (base case)

Figure 5-1. Level III trajectory for Tulsa, Oklahoma.

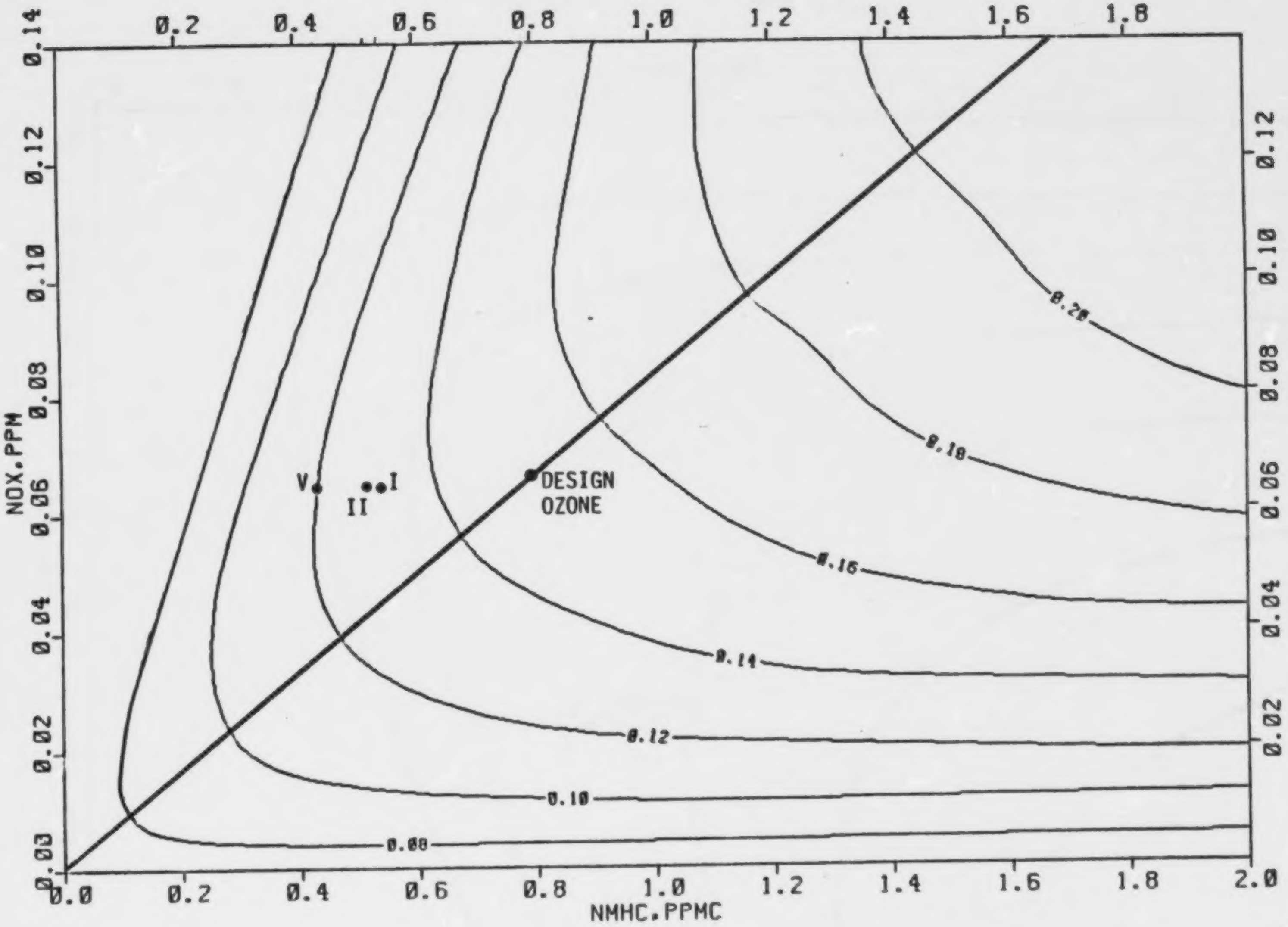
49r 81 3



(b) 29 July 1977 (base case)

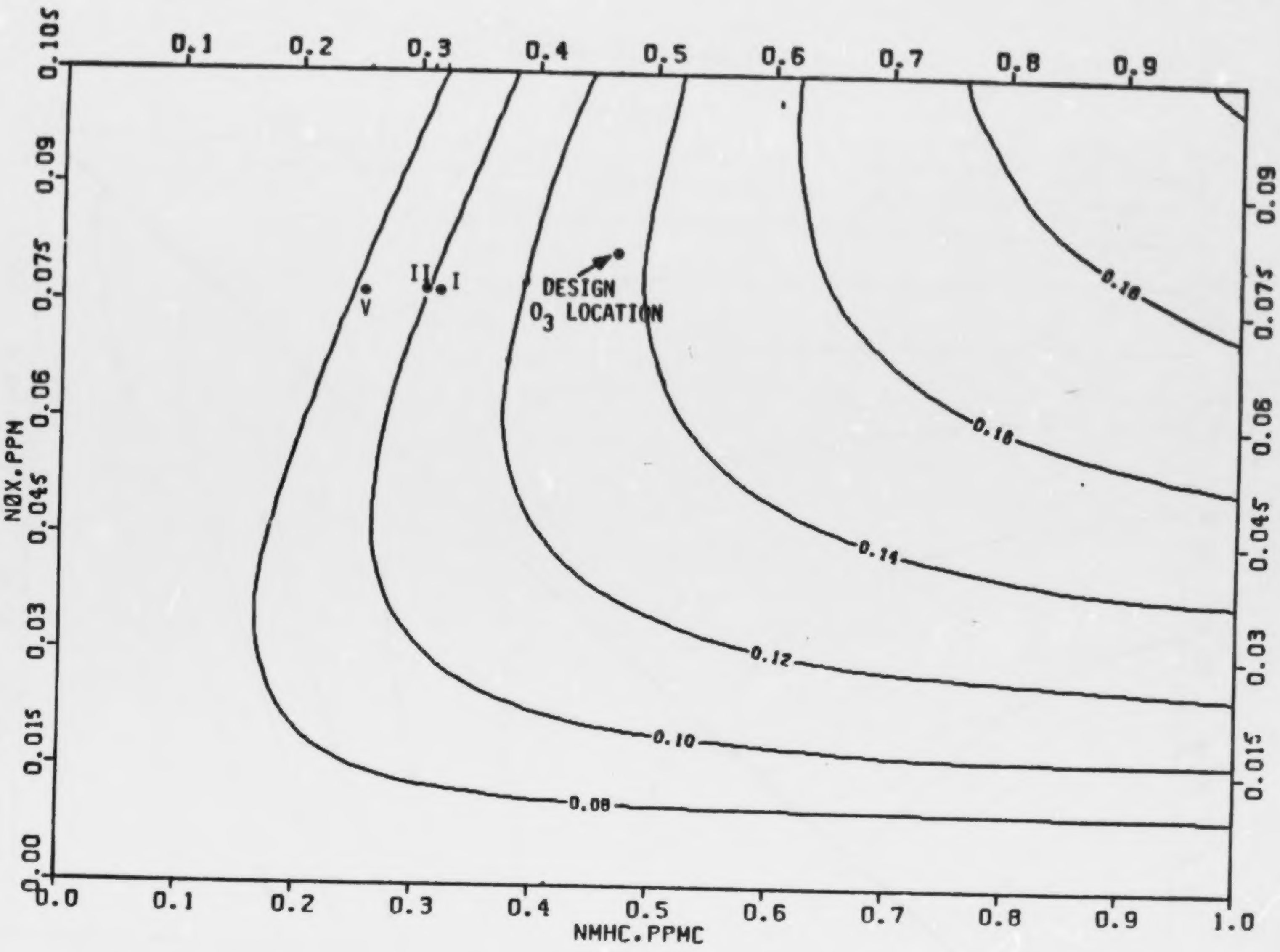
Figure 5-1 (Continued).

49r 81 3



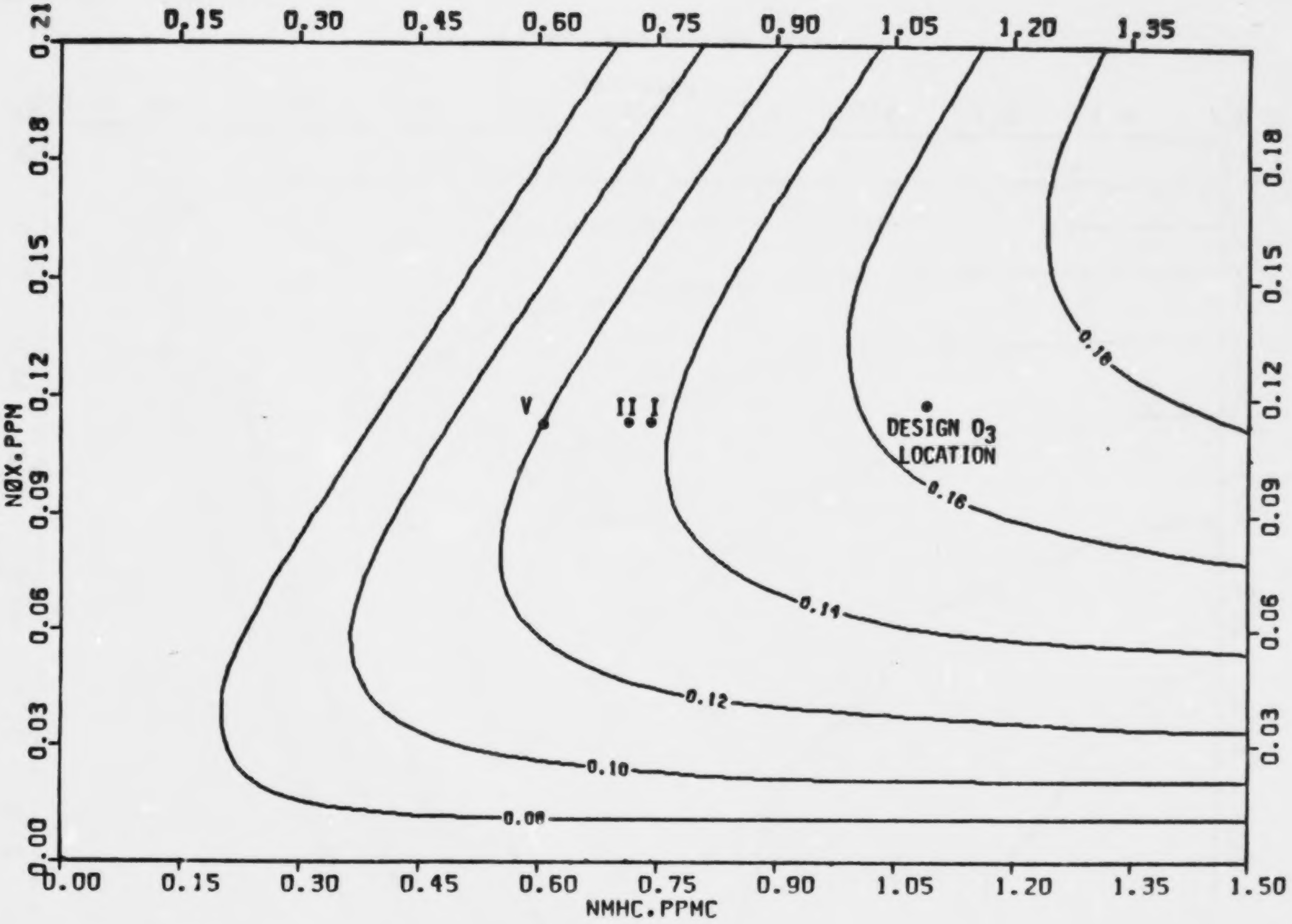
(c) 3 August 1977 (base case)

Figure 5-1 (Continued).



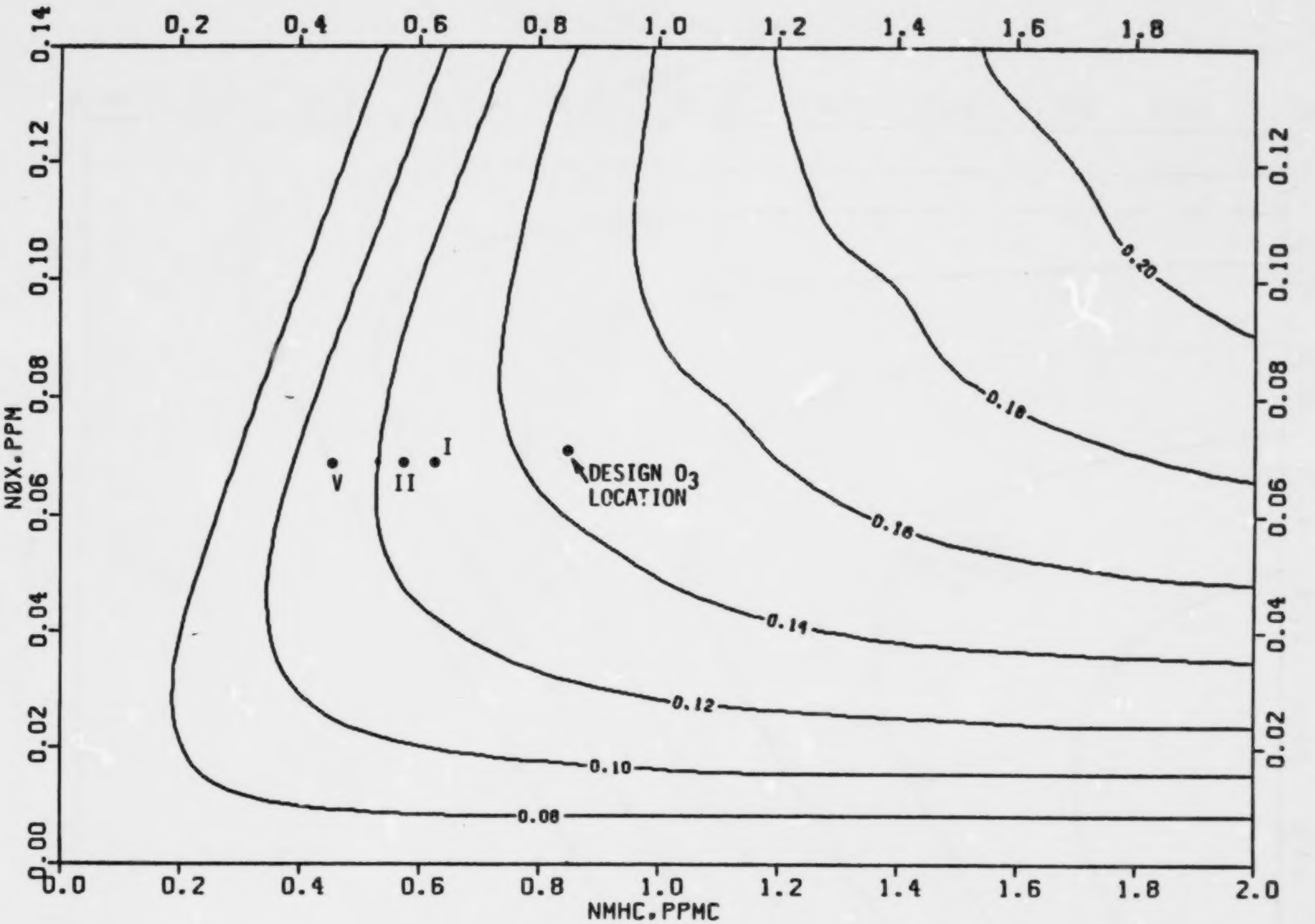
(d) 21 July 1987 (future year)

Figure 5-1 (Continued).



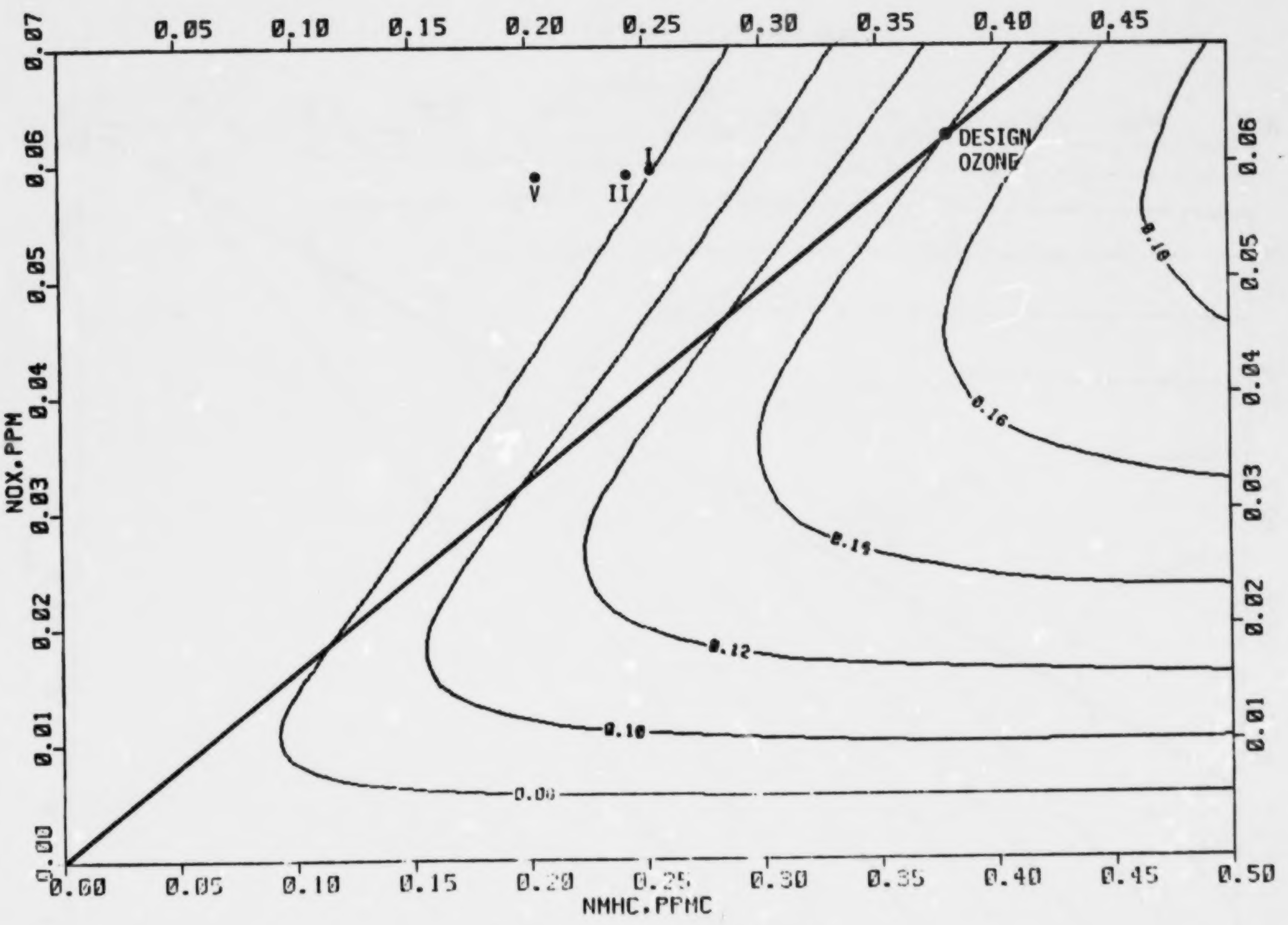
(e) 29 July 1987 (future year)

Figure 5-1 (Continued).



(f) 3 August 1987 (future year)

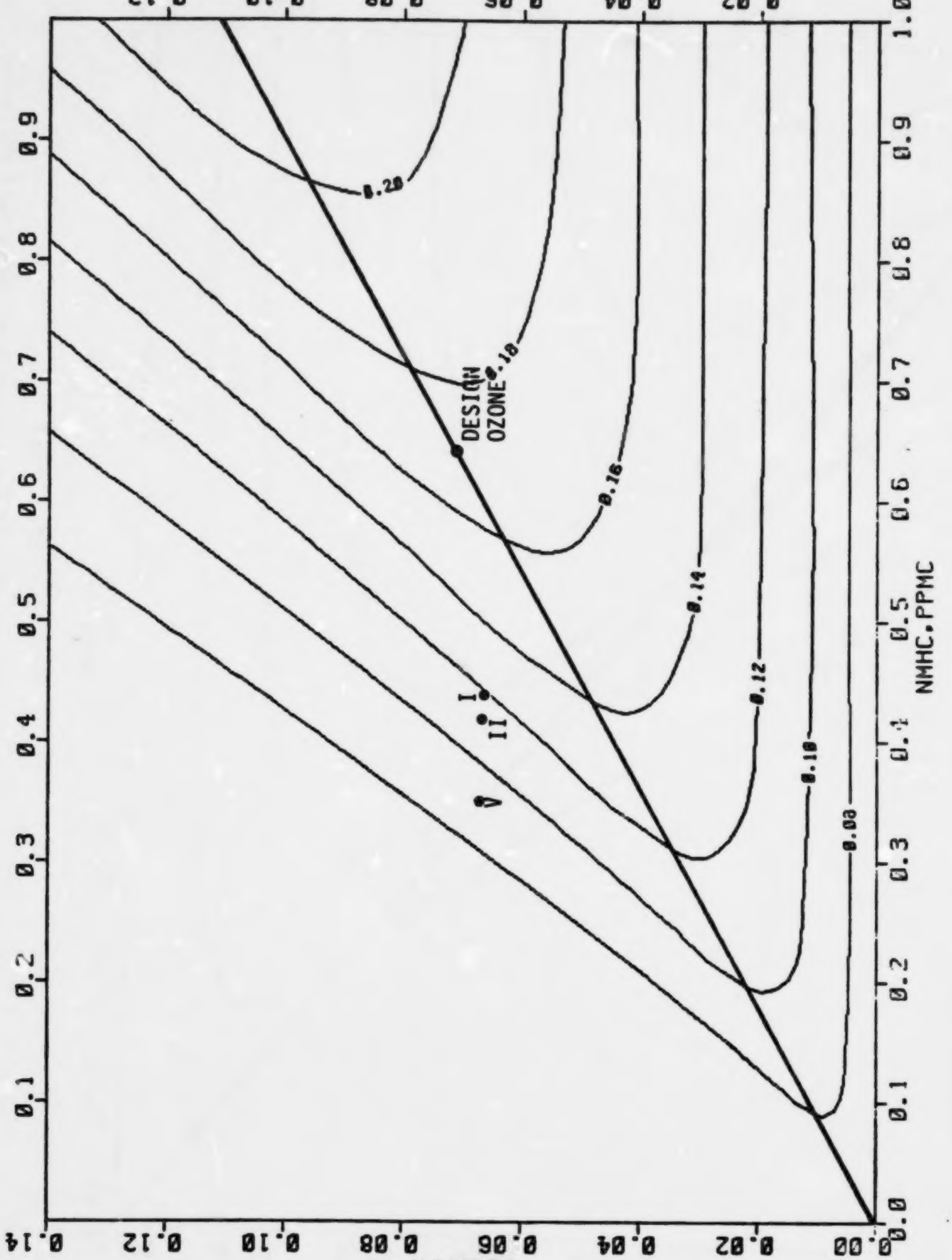
Figure 5-1 (Concluded).



(a) 21 July 1977 (base case)

Figure 5-2. Level III trajectory for Tulsa, Oklahoma using the Carbon-Bond Mechanism.

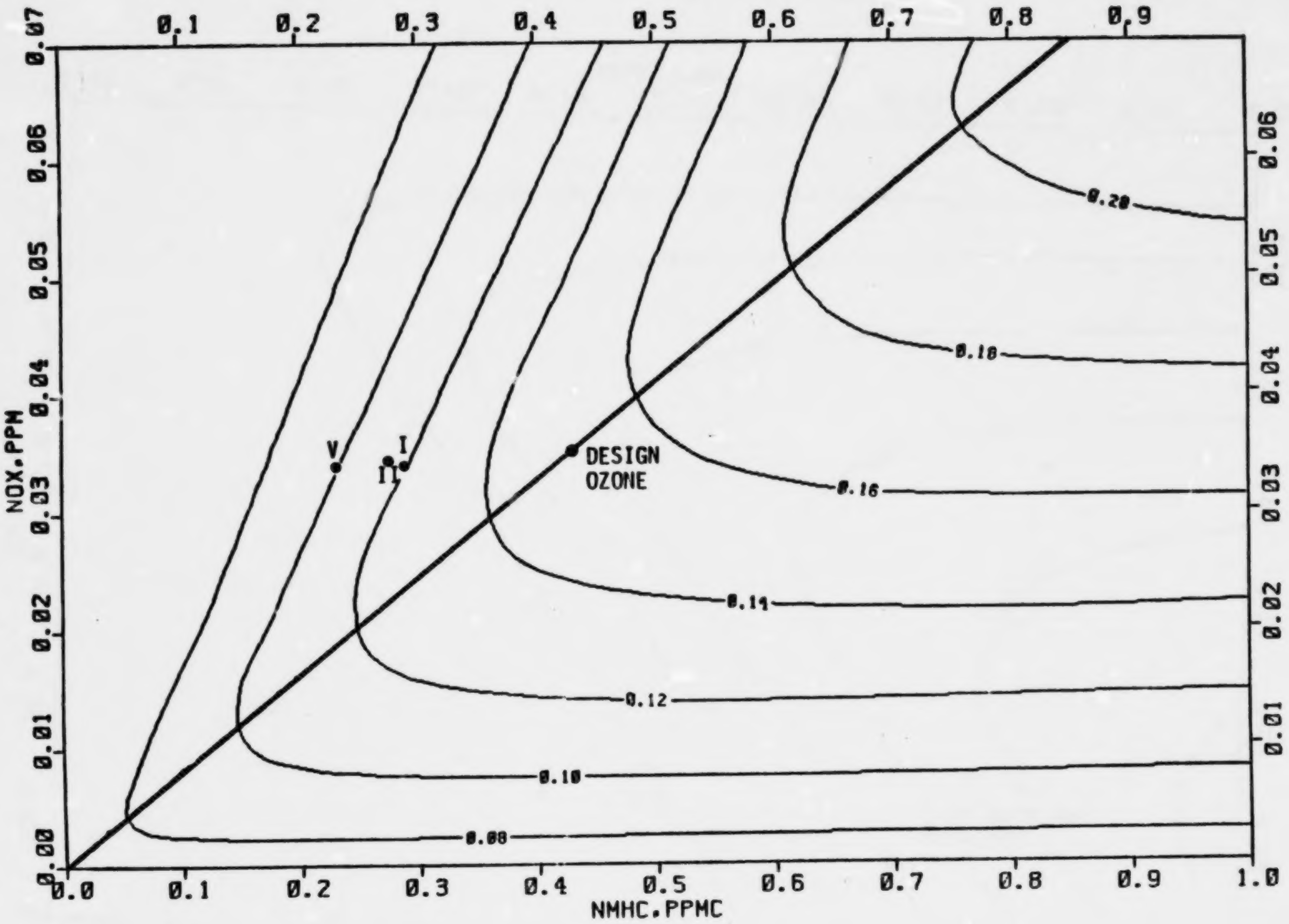
49r 81 3



(b) 29 July 1977 (base case)

Figure 5-2 (Continued).

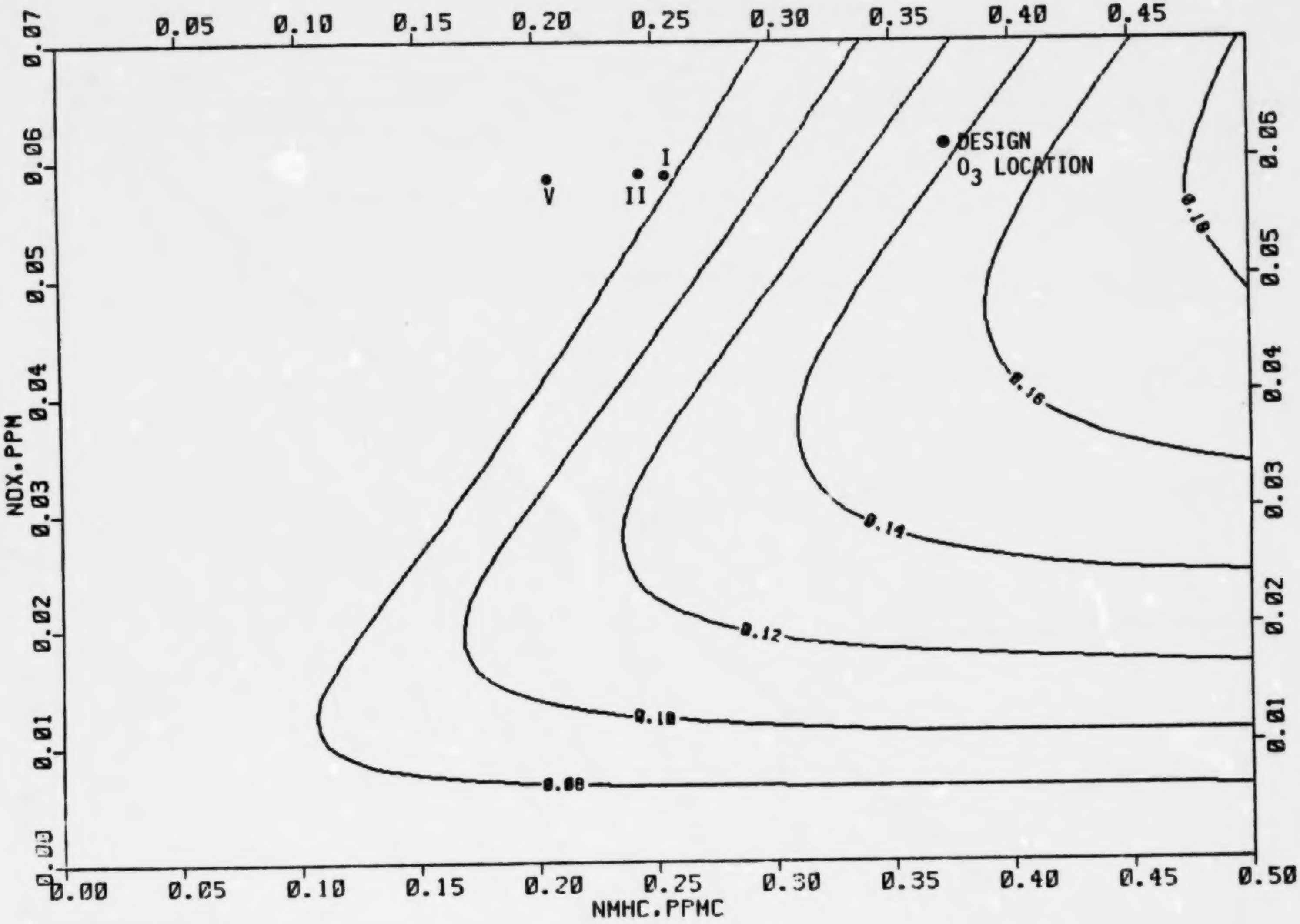
49r 81 3



(c) 3 August 1977 (base case)

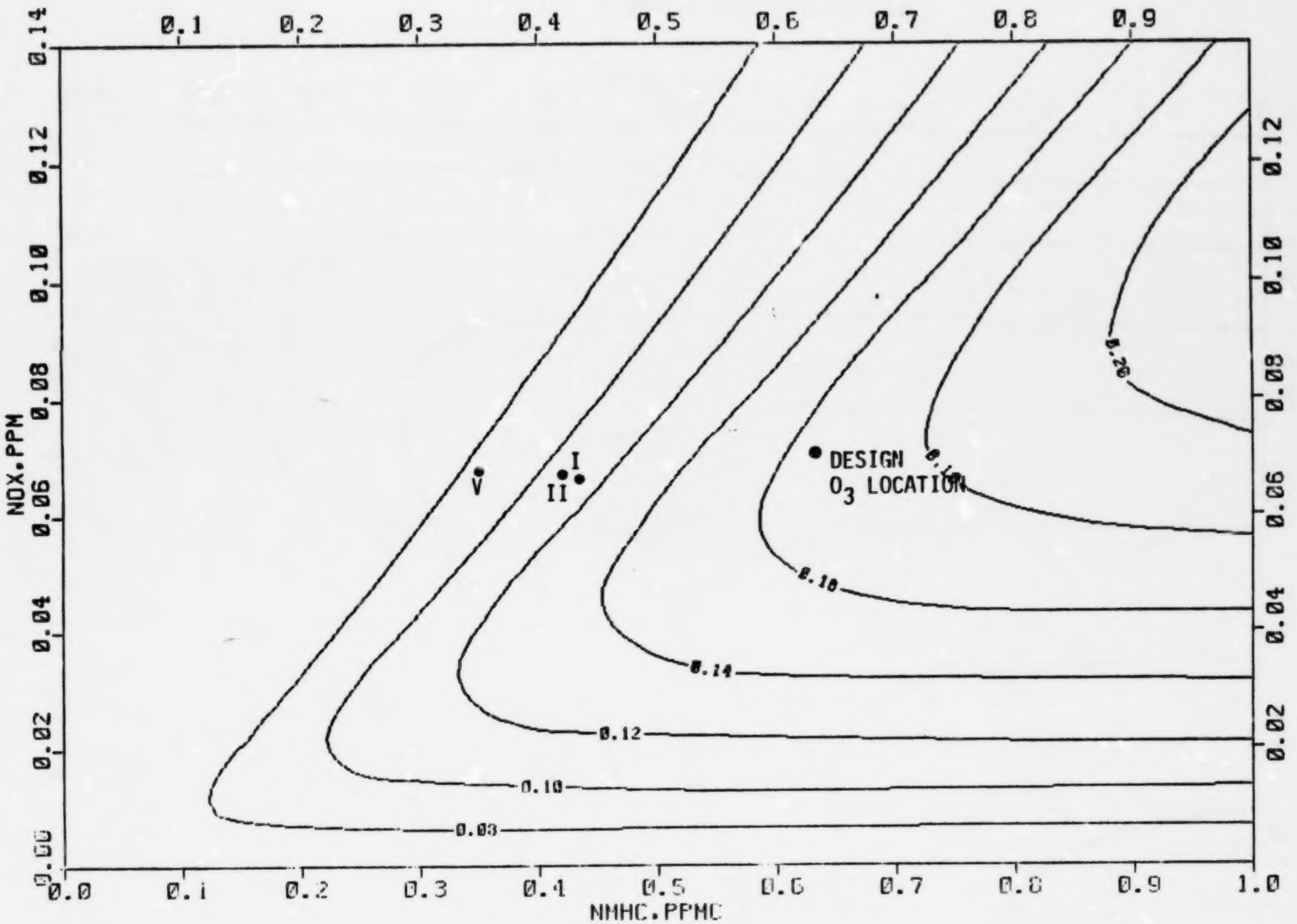
Figure 5-2 (Continued).

49I 81 3



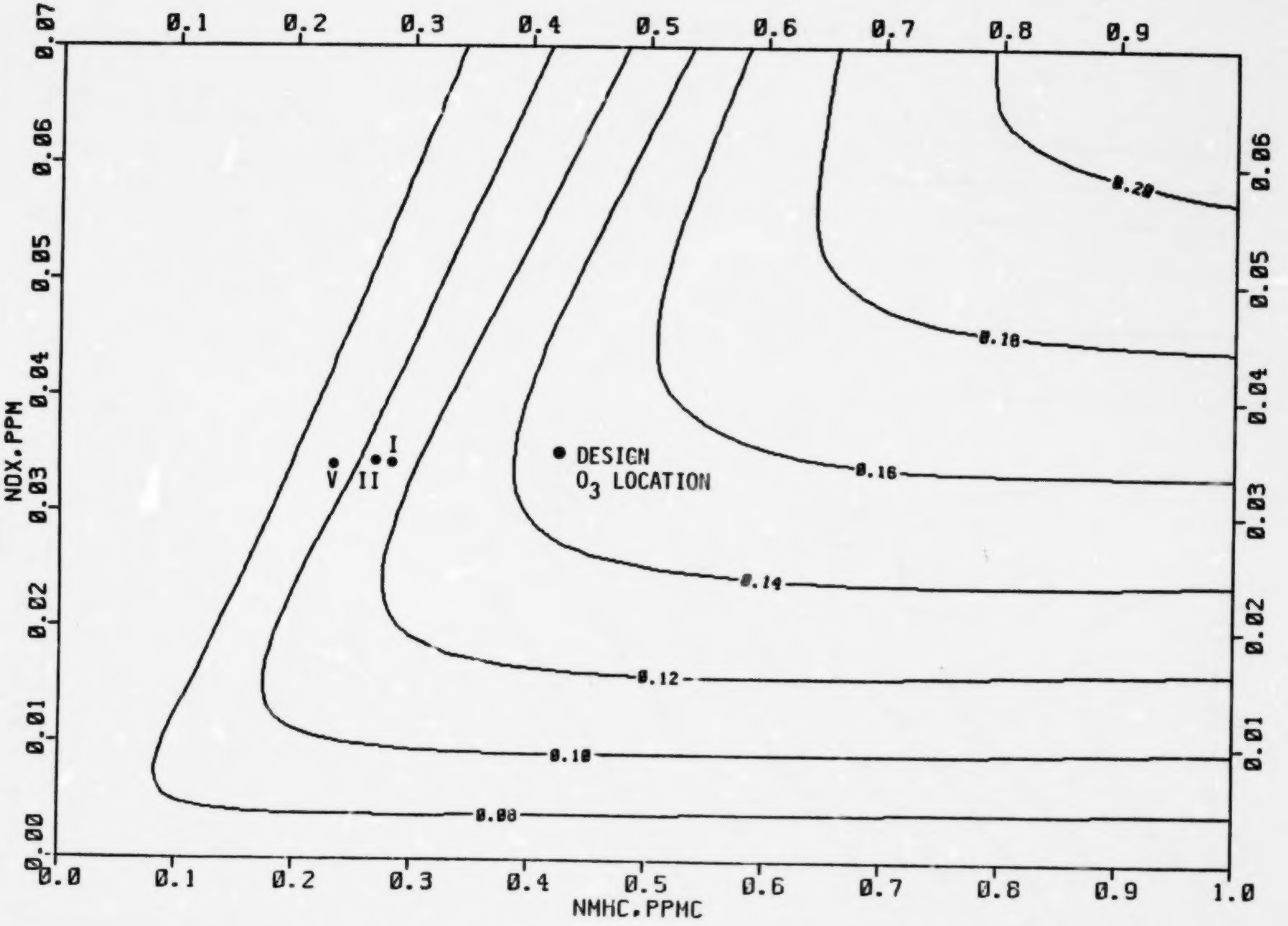
(d) 21 July 1987 (future year)

Figure 5-2 (Continued).



(e) 29 July 1987 (future year)

Figure 5-2 (Continued).



(f) 3 August 1987 (future year)

Figure 5-2 (Concluded).

TABLE 5-4. OZONE PREDICTIONS FROM VARIOUS MODELS FOR THE TULSA MODELING DAYS (lowered ozone aloft in the EKMA models) (ppm)

Date	SAI Airshed Model Results	Percentage* Change in Ozone	Level III EKMA Model Results	Percentage* Change in Ozone	Level III EKMA with CBM Model Results	Percentage* Change in Ozone
29 July 1977	0.17	0.0%	--	--	--	--
29 July 1987--option I	0.14	17.6	0.138	18.8%	0.11	35.3%
29 July 1987--option II	0.138	18.8	0.135	20.5	0.108	36.5
29 July 1987--option V	0.131	22.9	0.12	29.4	0.09	47.1
(observed O_3 = 0.17 ppm)						
21 July 1977	0.14	0.0	--	--	--	--
21 July 1987--option I†	--	--	0.102	27.1	0.08	42.9
21 July 1987--option II†	--	--	0.10	28.6	0.07	50.0
21 July 1987--option V†	-	--	0.08	42.9	0.05	64.3
(observed O_3 = 0.14 ppm)						
3 August 1977	0.12	--	--	--	--	--
3 August 1987--option I†	--	--	0.128	8.0	0.112	25.3
3 August 1987--option II†	--	--	0.125	10.0	0.108	28.0
3 August 1987--option V†	--	--	0.11	26.7	0.085	43.3
(observed O_3 = 0.15 ppm)						

---

[*] Percentage change in ozone $= \frac{(\text{Observed } O_3) - (\text{Predicted } O_3)}{(\text{Observed } O_3)} \times 100.$

[†] Airshed simulations for these days had not been performed at the time of the writing of this document.

TABLE 5-5. REQUIRED PERCENTAGE REDUCTIONS IN HYDROCARBON PREDICTED BY THE EKMA TO REACH 0.12 (ppm) OZONE LEVELS (3.7 percent NO_x reduction assumed)

Date--1977	Design O_3	Level III EKMA	Level III EKMA with CBM
21 July	0.14	17.0	10.7
29 July	0.17	44.6	28.1
3 August	0.15	37.6	28.2
2 September*		--	--

---

* Design ozone for this day was less than 0.12 ppm.

49r 81 13

percentage reductions 1.3 to 1.5 times those of the Level III EKMA using the Carbon-Bond chemistry to reach an ozone level of 0.12 ppm. Some reasons for this sensitivity are discussed in the next chapter; however, the main reason for the sensitivity appears to result from the 10-hour simulation time combined with the polarity of reactivity found in the 25-percent high reactivity propylene--the 75-percent low reactivity butane combination used in standard Level III EKMA. At similar overall ozone generation capacity, the two chemistries tend to produce different diurnal O_3 profiles as discussed in section 4. The high reactivity of propylene tends to cause the standard chemistry to make ozone faster than occurs with the CBM until the propylene runs out; then, ozone forms more slowly than the ozone generated by the CBM. The CBM has more levels of reactivity, which tend to even out the rate of ozone generations. However, with this more even rate of ozone generation, the CBM often produced simulations that did not reach an ozone peak within the 10 hours simulated by the OZIPM model. This lack of ozone peaking is exaggerated by conditions of low HC/NO_x ratio. Hence, the control scenarios that emphasize HC control tend to lower the HC/NO_x ratio and, in turn, the emphasis on ozone peaking results in high sensitivity. Thus, the standard mechanism peaks before the 10-hour cutoff point more often than it does in the CBM. Therefore, HC control using the CBM produces many ozone values taken during the last (of 10) hour by the OZIPM algorithm, even though the simulated ozone may still be rising rapidly in the model. Under similar conditions, the propylene/butane chemistry using 25-percent propylene could have produced an early peak that would perhaps be higher than the truncated peak produced by the CBM. Hence, longer simulation times may be required if the CBM were to be used in the EKMA.

SECTION 6

SENSITIVITY STUDIES

This section discusses four areas of sensitivity of the EKMA models to various input parameters and model characteristics investigated in this study:

- > Emission density information.
- > Ozone predictions obtained with the propylene/butane mechanism.
- > Surface and aloft precursor conditions.
- > Sensitivity of Level II EKMA models to the choice of the trajectory path.

SENSITIVITY OF THE EKMA MODEL TO EMISSIONS DENSITY INFORMATION

Emission densities with a 2-kilometer spatial resolution were originally developed by Engineering Science (1979); in the Airshed modeling effort, the grid cell size was increased to 4 kilometers. A recent study of the San Francisco region (Whitten, Hogo, and Johnson, 1981), concluded that the size of the grid cells can become important in the EKMA predictions if sharp differences are seen in adjacent grid cells. Ozone predictions can change significantly depending upon the emission fractions used in the calculations. In an effort to test the sensitivity of the EKMA model to grid resolution, we defined two trajectories parallel to the original trajectory, which had been defined to reach the maximum observed ozone for the 21 July 1977 modeling day. Figure 6-1 shows the two new trajectories (one east and one west of the original trajectory).

The SAI trajectory model predicted similar results for ozone concentrations from the eastern trajectory (0.145 ppm ozone) and the original trajectory (0.154 ppm ozone), whereas predictions from the western

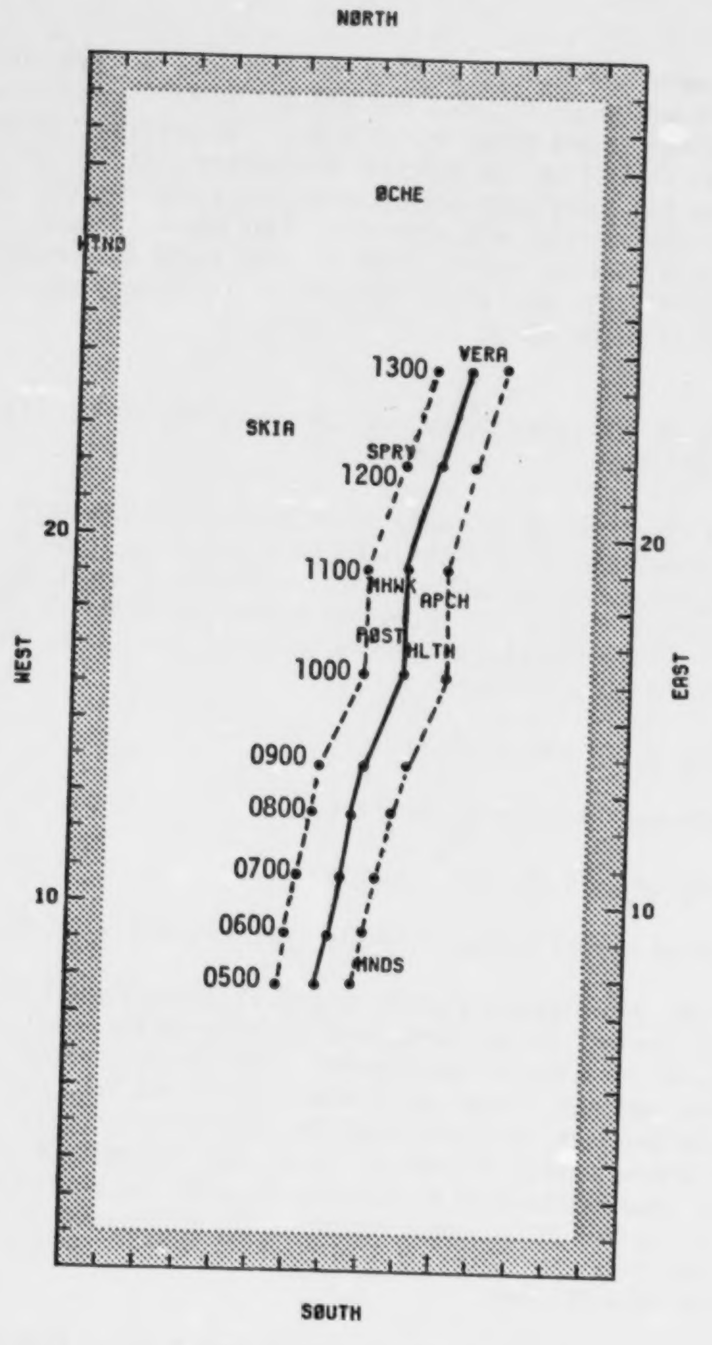

NORTH
OCHE
WIND
1300
VERA
SKIA
SPRY
1200
20
20
1100
MHWK
APCH
ROST
HLTH
1000
WEST
EAST
0900
0800
0700
10
10
0600
0500
MNDS
SOUTH

Figure 6-1. Trajectory paths used in the EKMA sensitivity study of grid resolution for 21 July 1977.

49r81 20

trajectory were lower (0.127 ppm). The emissions patterns for the new trajectories are shown in table 6-1 and the initial conditions for all three trajectories are shown in table 6-2. By averaging emissions and initial conditions from the original trajectory with the one next to it we also created two additional trajectories twice the original grid size. Performing EKMA calculations with these last two trajectories, we found that both gave similar results. The western trajectory resulted in an ozone value of 0.151 ppm, while the eastern trajectory resulted in an ozone value of 0.158 ppm.

SENSITIVITY OF THE PROPYLENE/BUTANE CHEMISTRY DUE TO VARIATION IN RATE CONSTANTS

Since its formulation, many of the rate constants used in the original propylene/butane mechanism (Dodge, 1978) have been updated with more recent measurements and evaluations (Atkinson and Lloyd, 1980). To test the sensitivity of the propylene/butane mechanism to rate constant changes, we investigated the effects on ozone predictions of perturbations in the following rate constants:

- NO_2 photolysis constant
- Aldehyde photolysis constants
- Radical and NO_x sink reactions
- Reactions of peroxy radicals (RO_2 and HO_2) with NO.

The NO_2 photolysis constant is calculated using a theoretical absorption curve. In the Tulsa monitoring program, total solar radiation was measured in units of langleys/min that can be related to the NO_2 photolysis constant. From these measurements and from the theoretical NO_2 photolysis constant, we found that the theoretical constant used in the EKMA was approximately 10 percent lower than the measured values. Table 6-3 shows results obtained by raising the EKMA NO_2 photolysis constant 10 percent using the 21 July meteorology. The difference in the ozone predictions is approximately a 3 percent increase from the base case ozone prediction of 0.096 ppm.

The photolysis of aldehydes can be important in photochemical smog mechanisms. The propylene/butane mechanism has a higher rate of aldehyde photolysis than the CBM. To estimate the differences in ozone predictions caused by aldehyde photolysis, we lowered the aldehyde photolysis rates in the propylene/butane mechanism so that the two mechanisms would correspond

TABLE 6-1. EMISSIONS RATES FOR TRAJECTORIES PARALLEL TO THE ONE TO VERA FOR 21 JULY 1977

Time (CDT)	Trajectory West of Vera HC (ppmC/hr)	Trajectory East of Vera HC (ppmC/hr)
0500-0600	0.0006	0.0014
0600-0700	0.0008	0.004
0700-0800	0.0222	0.017
0800-0900	0.0130	0.0391
0900-1000	0.0285	0.0789
1000-1100	0.5983	0.9088
1100-1200	0.3207	0.2386
1200-1300	0.0218	0.027

Time (CDT)	Trajectory West of Vera NO_x (ppm/hr)	Trajectory East of Vera NO_x (ppm/hr)
0500-0600	0.0	0.0007
0600-0700	0.0	0.0015
0700-0800	0.0003	0.0052
0800-0900	0.0016	0.0046
0900-1000	0.0067	0.0128
1000-1100	0.1054	0.0924
1100-1200	0.0633	0.0621
1200-1300	0.0078	0.009

49r 81 20

TABLE 6-2. INITIAL CONDITIONS USED IN THE EKMA CALCULATIONS FOR 21 JULY 1977

Surface

Trajectory West of Vera			Trajectory to Vera	Trajectory East of Vera
NO	0.00001	ppm	0.00001	0.00001
NO_2	0.0031	ppm	0.0031	0.0032
NO_x	0.0031	ppm	0.0031	0.0032
NO_2/NO_x	0.9968	ppm	0.9968	0.9969
OLE	0.0029	ppmC	0.0029	0.0029
PAR	0.0643	ppmC	0.0643	0.0643
ARO	0.0720	ppmC	0.072	0.0720
ETH	0.0115	ppmC	0.0115	0.0115
CARB	0.0120	ppmC	0.012	0.0120
HC	0.1627	ppmC	0.1627	0.1627
O_3	0.0354	ppm	0.0356	0.0349
CO	0.1000	ppm	0.1000	0.1000

Aloft

Trajectory West of Vera		Trajectory to Vera	Trajectory East of Vera
NO	0.0001	0.0003	0.0004
NO_2	0.0011	0.0016	0.0022
NO_x	0.0012	0.0019	0.0027
OLE	0.0015	0.0013	0.0012
PAR	0.0611	0.0587	0.0582
ARO	0.0559	0.0488	0.0482
ETH	0.0098	0.0090	0.0089
CARB	0.0136	0.0149	0.0158
HC	0.1419	0.1329	0.1323
O_3	0.0613	0.067	0.07
CO	0.8158	1.4778	1.9453

TABLE 6-3. LEVEL II EKMA OZONE PREDICTIONS USING THE PROPYLENE/BUTANE CHEMISTRY FOR 21 JULY 1977 UNDER VARIOUS CONDITIONS (OBSERVED OZONE = 0.14 PPM)

Sensitivity Run	Predicted Ozone (ppm)
Base case	0.096
Raised NO_2 photolysis = 10 percent	0.099
Raised NO_2 photolysis and lowered aldehyde photolysis = 60 percent	0.093
Raised RO_2 + NO reactions to a ratio of 0.86 with OH + NO_2 reaction	0.131

49r 81 16

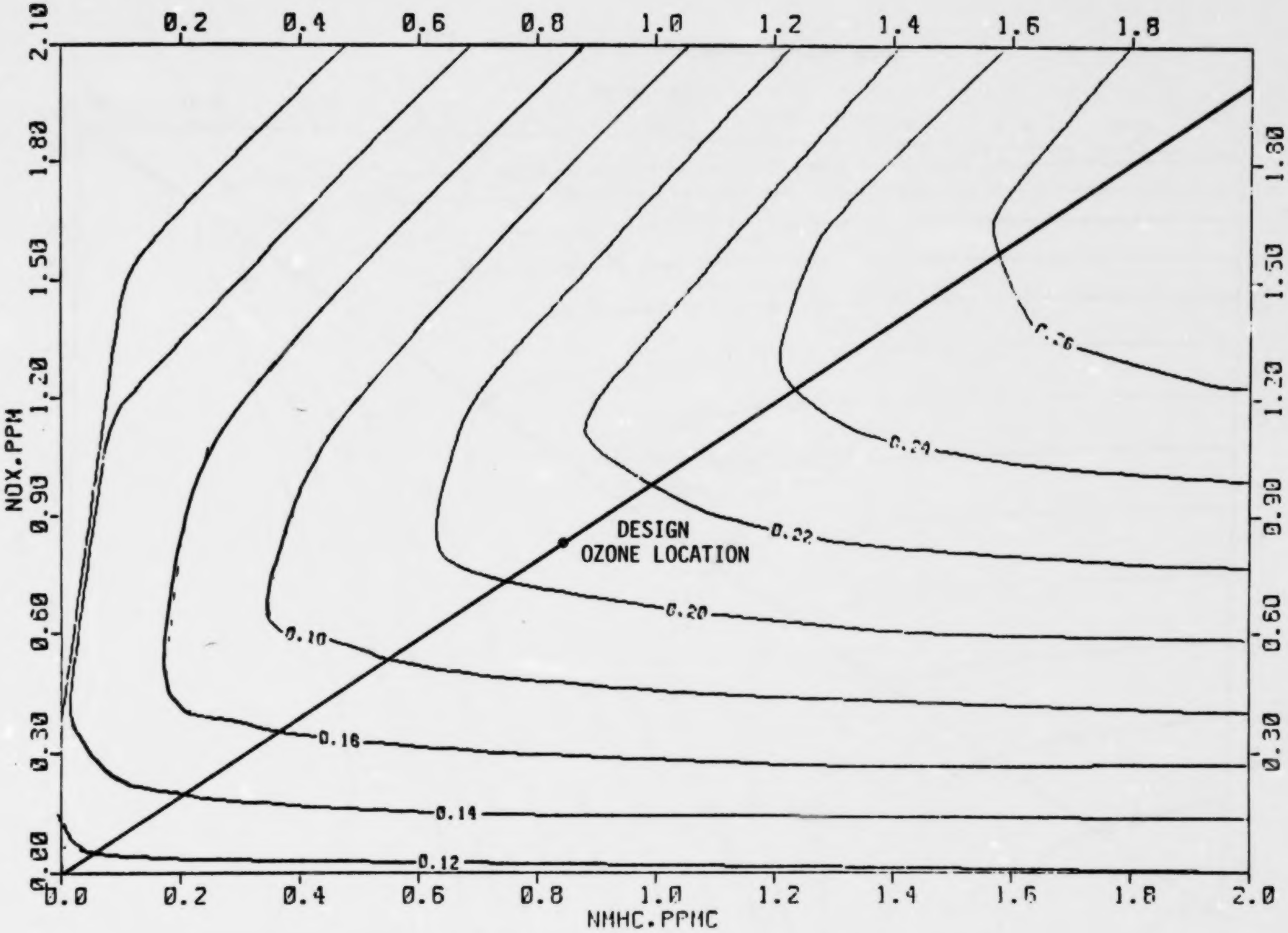
at 1100 CDT. To make the chemistry of the propylene/butane and Carbon-Bond mechanisms as similar as possible, we kept the NO_2 photolysis rate increased by 10 percent for both mechanisms. From the results of this exercise shown in table 6-3, we see that the predicted ozone is approximately 3 percent lower than the base case value when the aldehyde photolysis rates are lowered by 60 percent.

A third area of difference between the two photochemical smog mechanisms concerns the peroxy radical reactions that convert NO to NO_2 (i.e., RO_2 + NO reactions). We performed a sensitivity test by raising the RO_2 + NO reactions to 6900 $ppm^{-1}min^{-1}$ from the 1200 to 1800 $ppm^{-1}min^{-1}$ value normally used. The significant factor in these kinetics is found in the ratio of ozone production, which takes place through the conversion of NO to NO_2 by the peroxy radicals, to the loss of both radicals and NO_x via the nitrate production caused by the hyroxyl radical reaction with NO_2. In the CBM, this ratio is 0.86; therefore, using a value of 6900 $ppm^{-1}min^{-1}$ in the propylene/butane mechanism for all reactions of the type RO_2 + NO would bring the ratio up from about 0.2 to 0.86.

Results of this exercise are also shown in table 6-3. As we can see, the predicted ozone values increased by approximately 36 percent over the base case value. The predicted ozone value of 0.13 ppm is much closer to the observed value of 0.14 ppm for both the 21 July day and the CBM/OZIPM predicted value of 0.15 ppm. Thus, we see that updating the RO_2 + NO reaction rates can provide one explanation for the low simulated ozone concentrations predicted by the propylene/butane mechanism. Although changing this one type of reaction provided an explanation for much of the difference routinely seen between the results obtained from the CBM and the propylene/butane mechanism, this change should not be construed as the means to easily update the propylene/butane mechanism for use in EKMA applications. Before an updated version of the mechanism can be used, a revalidation against smog chamber data must be performed.

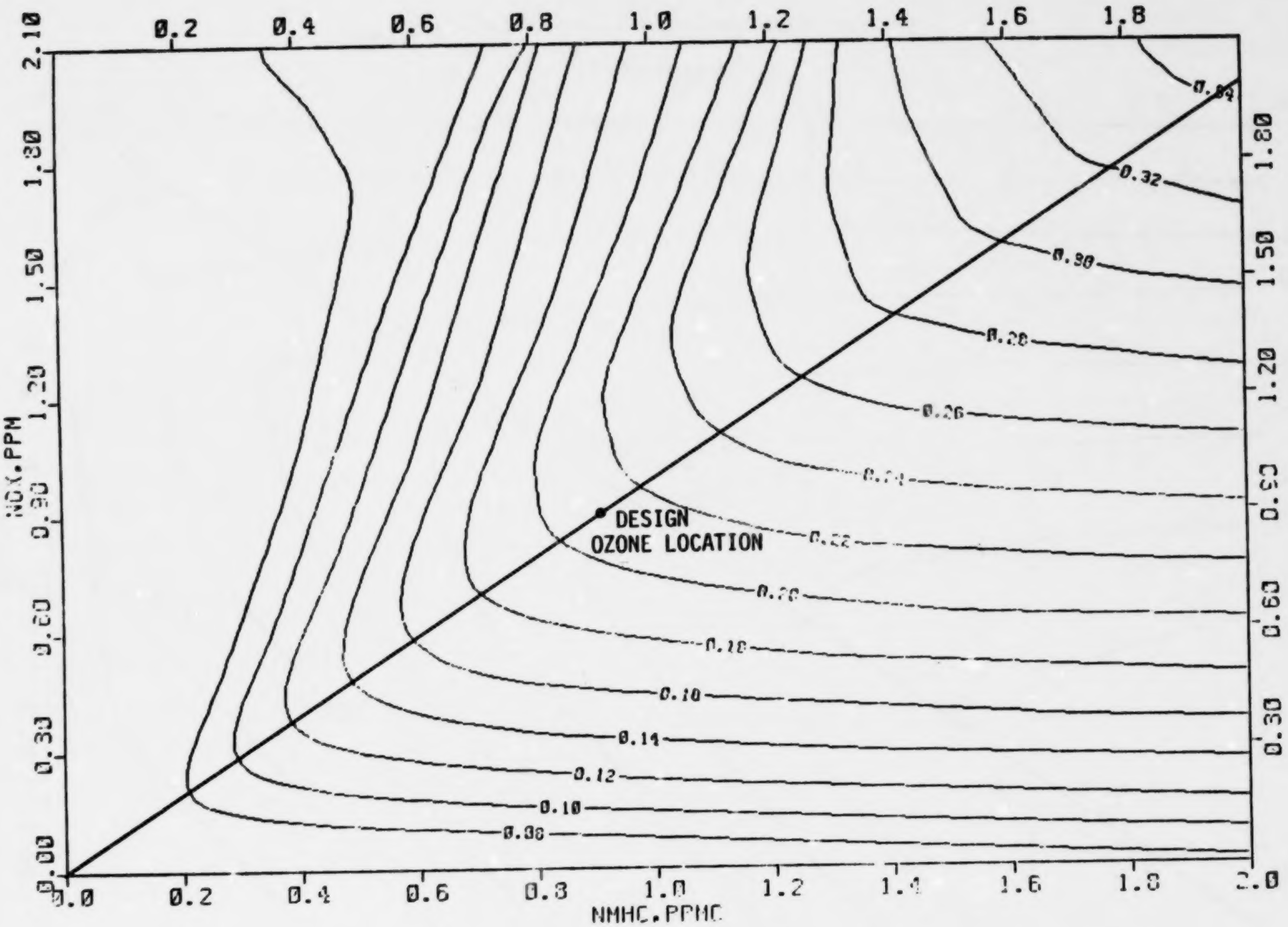
SENSITIVITY OF MODELS TO HYDROCARBON AND NO_X BACKGROUND CONCENTRATIONS

In the original Airshed Model study of the Tulsa area, it was believed that the base year hydrocarbon concentration of 0.2 ppmC represented typical and insignificant background values. Thus, it was felt that the future year simulations would not require reduced initial and aloft hydrocarbon concentrations. However, it was later determined that the hydrocarbon concentrations found in the Tulsa region are as low as 0.04 ppmC. CBM/OZIPM isopleths generated to assist the original Airshed modeling effort predicted that a hydrocarbon reduction of 94 percent might be required to achieve the federal ozone standard of 0.12 ppm from the highest simulated ozone level [figure 6-2(a)] if the 0.2 ppmC level



(a) Background Hydrocarbons Held Constant

Figure 6-2. CBM-EKMA Oklahoma simulation of 20 July 1987--trajectory to the regional ozone maximum.



(b) Background Hydrocarbons Rolled Back

Figure 6-2 (Concluded).

existed. The isopleth diagram was generated using the emissions and meteorology of the specific trajectory to the maximum predicted ozone of 0.21 ppm from the base case Airshed Model simulation. A monitoring site was not located at the site of this maximum occurrence. The OZIPM computer code was set up to keep the initial conditions for each calculation constant and to vary only the emissions.

A second isopleth was generated using these same inputs, but initial and aloft conditions were allowed to vary proportionally with the emissions changes [figure 6-2(b)]. In the guidelines for the use of the standard city-specific EKMA, the initial and aloft precursor concentrations are referred to as "transported" pollutants in the surface and aloft layers. Varying the concentration proportionally with the emissions reductions on the isopleth diagram certainly represents an extreme case, since some natural and transported pollutants would not vary between base and future years. However, the use of fixed concentrations for these background pollutants represents the other extreme. The two approaches tend to bracket the problem. For many urban areas, there is undoubtedly some carry-over--or return of previously emitted, but unreacted--precursors. Surely, the level of such pollutants would be reduced according to the level of local controls. Additionally, numerous controls (e.g., those for automobile-related emissions) are common to all urban areas because of federal regulations, and some of the pollutants transported from upwind sources would vary in proportion to local controls. However, all of these background pollutants can vary only between present levels and some natural, and currently uncertain, background level.

For the diagram using modified background concentrations, an estimated hydrocarbon reduction of only 53.8 percent is needed for attainment of the ozone standard. The primary reason for the considerable difference between the two isopleths in this case is that the initial conditions dominate emissions in the total precursor concentration for the simulations. This situation is unlike that of the Los Angeles simulations in which the emissions tend to dominate the modeling region (Whitten and Hogo, 1981).

To further exemplify the importance of the initial and aloft conditions in the Tulsa simulations, we used the SAI trajectory model to simulate several sensitivity runs in which the hydrocarbon and NO_x concentrations in the surface and aloft layers were varied. For a base case, we used the trajectory to the maximum ozone predicted by the Airshed Model. In each of the runs, we lowered the hydrocarbon and/or NO_x by 50 percent. The results, presented in table 6-4, show that the hydrocarbon concentrations are the key pollutant. It should also be noted that the surface concentrations were changed only at the 0500 starting time of the model; by the normal EKMA starting time of 0800, the 50 percent change in the mixing layer concentration still amounted to a 42 percent reduction.

TABLE 6-4. SAI TRAJECTORY MODEL RESULTS OBTAINED BY VARYING HYDROCARBON AND NO_x CONCENTRATIONS IN THE SURFACE AND ALOFT LAYERS

Concentration Level	Predicted Ozone (ppm)
Base case	0.21
Hydrocarbon reduced by one-half	0.174
NO_x reduced by one-half	0.21
Both hydrocarbon and NO_x reduced by one-half	0.174

We also investigated the sensitivity of ozone prediction to the addition of precursor transport for the CBM/OZIPM and Level-III-type EKMA models. For the CBM/OZIPM model, we cut the aloft hydrocarbons in half while keeping the surface hydrocarbons at the original values (see section 3). This change reflects the observed measurements more closely. The average aloft hydrocarbon concentrations were approximately half those found in the surface bag samples (see section 3). Results obtained using the lower hydrocarbon concentrations aloft for the 29 July 1977 day are shown in table 6-5. We see that the ozone maximum was reduced by 13 percent as the result of a 50 percent HC reduction aloft. For the Level III EKMA models, no precursor transport (except ozone) was considered in the previous sections. Current Level III guidelines (EPA, 1980) do not recommend using surface and aloft precursor transport for normal applications unless the user decides otherwise. To test the sensitivity of the Level III EKMA models to precursor transport, we developed averaged surface and aloft hydrocarbon transport as inputs for the 29 July 1977 day.

On the basis of procedures outlined in appendix B of the Level III guidelines (EPA, 1980), we determined the mean contribution factor of the Liberty Mounds station on the urban core by comparing 0600 to 0900 observed NMOC between the Liberty Mounds station with the two monitoring stations located in the urban core. Results of this comparison are presented in table 6-6, which shows only complete NMOC samples. When NMOC samples are reported for both urban stations, an average is taken between the two stations. From these comparisons, we found the median contribution factor to be 0.36. This factor times the 0600 to 0900 average NMOC used for each modeling day gives the NMOC precursor in the surface layer. NO_x contribution factors were also determined for the same days for which there were calculated NMOC contribution factors. The results of this exercise are shown in table 6-6(a). The median contribution factor is 0.044. From the Level III guidelines, we readjusted the post-0800 emissions by 1.0 minus the median contribution factors. Aircraft samples were made between 26 August and 17 September 1977 for hydrocarbon, NO_x, and ozone. Table 6-7 shows aircraft measurements of NMOC at different altitudes taken in the area around Liberty Mounds (figure 6-3) during the morning hours. From the aircraft data, we averaged the measurements taken at the 1200-ft and 2500-ft level to determine the average NMOC and NO_x aloft. Of the six days of aircraft measurements, all observations were fairly consistent except for those of 2 September. The NO_x measurements were on the average twice as high as the measurements observed on the other days. The hydrocarbon measurements were approximately 50 to 75 times higher on 2 September than on any of the other days. The average NMOC aloft is 0.062 ppmC (not including the 2 September measurements) and 0.002 ppm for NO_x aloft (not including the 2 September measurements). If all the measurements are averaged, the NMOC could be 0.452 ppmC and NO_x

TABLE 6-5. EFFECT OF PRECURSOR CONDITIONS ON OZONE PREDICTIONS FOR 29 JULY 1977 FOR THE CBM/OZIPM AND LEVEL III EKMA MODELS

Model	Predicted Ozone (ppm)
CBM/OZIPM (base case)	0.15
CBM/OZIPM (hydrocarbon aloft reduced by one-half)	0.13
Level III EKMA (base case)	0.12
Level III EKMA (added surface and aloft percursors)	0.13

49r 81 16

TABLE 6-6. CALCULATION OF THE CONTRIBUTION FACTORS OF TRANSPORTED POLLUTANTS TO URBAN LEVELS--1977[*]

(a) NO_x
(ppm)

Date	Liberty Mounds	Post Office	Health Department	Contribution Factor[†]
21 August	0.008	0.024	0.022	0.360
22 August	0.012	0.102	0.097	0.124
12 September	0.002	0.082	0.054	0.037
16 September	0.003	0.124	0.129	0.023
25 September	0.004	0.050	0.028	0.143
26 September	0.004	0.090	0.090	0.044
27 September	0.002	0.044	0.032	0.063
28 September	0.001	0.025	0.027	0.037

[†] Average contribution factor = 0.104; standard deviation = 0.112; median contribution factor = 0.044.

(b) NMOC
(ppmC)[§]

Date	Liberty Mounds	Post Office	Health Department	Contribution Factor[**]
22 July	0.536	--	--	--
23 July	0.327	--	--	--
21 August	0.277	0.767	--	0.36
22 August	1.042	3.684	1.127	0.43[*]
12 September	0.106	0.348	--	0.30
16 September	0.171	0.871	0.566	0.24[*]
18 September	0.068	--	--	--
25 September	0.121	0.390	--	0.31
26 September	0.279	0.653	0.516	0.48[*]
27 September	0.149	0.300	--	0.50
28 September	0.083	0.278	--	0.30
29 September	0.076	--	--	--

[§] Only complete hydrocarbon samples are presented.

[**] Average contribution factor = 0.365; standard deviation = 0.095; median contribution factor = 0.36.

---

[*] Contribution factors are calculated using the average of the values obtained for the post office and Health Department sites.

TABLE 6-7. AIRCRAFT MEASUREMENTS OF NMOC

Date	Time (CDT)	Altitude (ft)	NMOC (ppmC)
26 August 1977	0722	1200	0.0416
	0725	2500	0.0407
	0731	5000	0.0995
	0737	7550	0.0259
2 September 1977	0729	1100	3.114
	0736	2600	1.699
	0743	5000	2.134
	0752	7600	1.18
3 September 1977	0726	1250	0.097
	0731	2500	0.039
	0738	5000	0.0164
	0746	7700	0.0636
11 September 1977	0724	1500	0.0445
	0727	2500	0.0475
	0734	5000	0.0201
	0742	7500	0.0215
16 September 1977	0726	1500	0.0879
	0729	2700	0.0725
	0736	5000	0.0213
	0743	7500	0.0345
17 September 1977	0739	1500	0.0885
	0741	2500	0.0563
	0745	5000	0.095
	0751	7500	0.236

would be 0.003 ppm. We decided to use an NMOC value of 0.062 ppmC and a NO_x value of 0.002 ppm since the measurements of 2 September are questionable.

From the results of the exercise shown in table 6-5, we see that the predicted ozone maximum value was raised by 8 percent when the HC precursors were added.

The high sensitivity to the background HC levels assumed in the original SAI Airshed Model validation effort has been demonstrated in this study. This sensitivity applies to both the base case and control predictions. Largely as a result of this demonstration using the EKMA models and the SAI trajectory model, the study using the SAI Airshed Model is currently being reevaluated using a combination of more reactive emissions, fewer background hydrocarbons, and observations that have been adjusted downwind (to account for incorrect KI calibration) and shifted in time (to correct misinterpretations of daylight, rather than standard, time). These pending changes in the Airshed Model results do not necessarily invalidate the comparisons made to date between the Airshed Model and the various trajectory models studied here. The verifying factor in the comparisons conducted to date is the use of common data in the various models and, thus, the comparisons show differences in results accruing from differences in model formulation and implementation.

SENSITIVITY OF LEVEL II EKMA MODELS TO TRAJECTORY SELECTION INVOLVING WIND SHEAR

In this section, we discuss problems that can occur from the use of trajectory-specific emissions for days with significant wind shear. As noted in the previous discussion of the ozone predictions for the 29 July 1977 day, the SAI trajectory model results (and consequently, the CBM/OZIPM EKMA models results) do not agree with those of the SAI Airshed Model. This lack of agreement is apparently related to wind shear during the early morning hours. Figure 6-3 shows the two trajectory paths used for the SAI trajectory model calculations. One trajectory path is based on the surface-level wind fields, whereas, the other is based on an average of the first- (surface) and second-level winds. We see from figure 6-3 that the trajectories are significantly different during the hours from 0500 to about 1000 CDT; yet after 1000 CDT, the trajectory paths are quite similar.

The SAI trajectory model predicted ozone concentrations of 0.14 ppm from both of the trajectory paths, and the Airshed Model predicted an ozone value of 0.17 ppm. We note that the two trajectory paths represent two extremes in terms of the possible trajectory taken by air flowing in

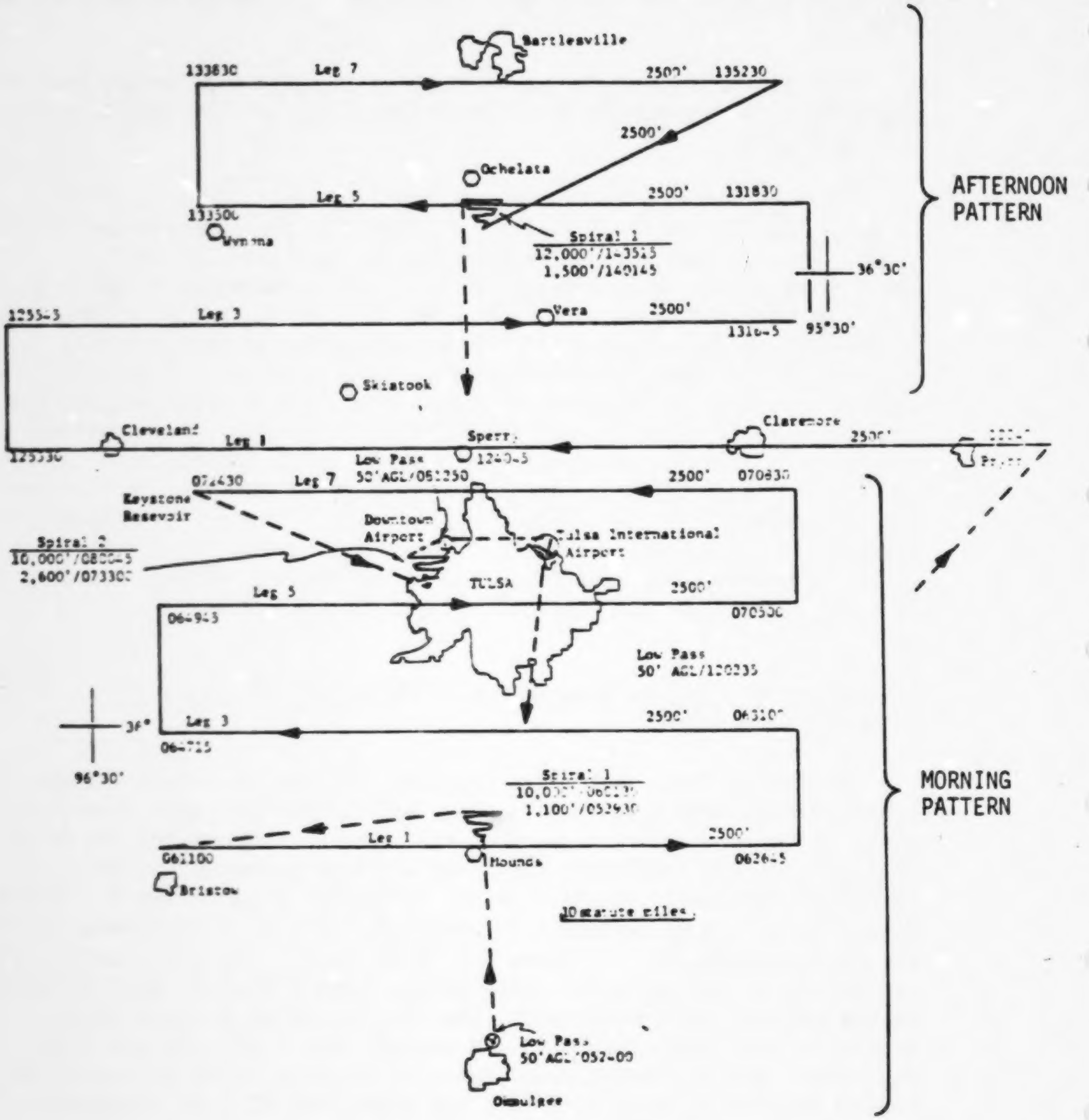

Bartlesville
133830
Leg 7
2500'
135230
2500'
Ochelata
Leg 5
2500'
131830
133500
Wynona
Spiral 1
12,000'/143515
1,500'/140145
36°30'
125545
Leg 3
Vera
2500'
131645
95°30'
Skiatook
Cleveland
Leg 1
Sperry
Claremore
2500'
125330
124045
Pryor
Low Pass
50'AGL/051250
072430
Leg 7
2500'
070830
Keystone
Reservoir
Downtown
Airport
Tulsa International
Airport
Spiral 2
10,000'/080045
2,600'/073300
TULSA
Leg 5
2500'
064945
070500
Low Pass
50' AGL/120235
36°
Leg 3
2500'
063100
064715
96°30'
Spiral 1
10,000'/060130
1,100'/052930
Leg 1
2500'
061100
Mounds
062645
Bristow
10 statute miles
Low Pass
50'AGL/052400
Okmulgee
AFTERNOON PATTERN
MORNING PATTERN

Figure 6-3. Typical transport flight pattern.

49r 81 20

the Airshed Model. The appropriate average path, one comparable to the Airshed Model simulations, would be somewhere between the two paths shown in figure 6-3 for the early-morning hours. The critical factor in path selection is the gridded emission inventory. If the grid squares with high emissions are bypassed, the model will not have sufficient precursor concentrations to generate the proper ozone level. In the present case, all emissions between these two path extremes contribute to the air parcel that finally forms at 1000 CDT and moves to the monitoring site. This area is illustrated by the shaded portion of figure 6-4.

Figure 6-5 shows the spatial distribution of emissions of reactive hydrocarbons during the hour from 0800 to 0900 CDT. From this figure we see that the two specific trajectories used in the SAI trajectory model calculations did not pick up the high emissions located in cell (6, 17).

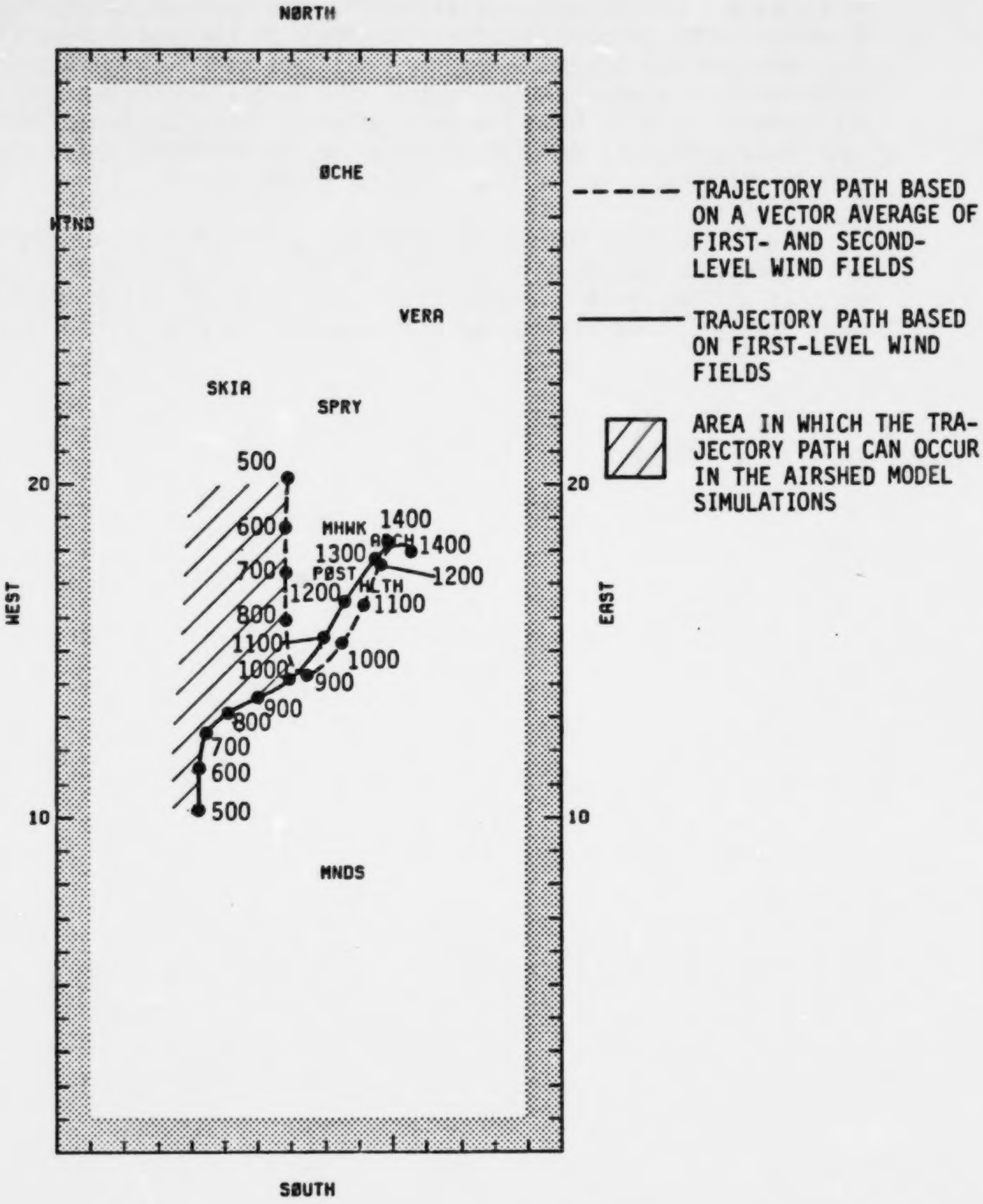

NORTH
OCHE
WIND
VERA
SKIA
SPRY
MHWK
ARCH
POST
HLTH
MNDS
WEST
EAST
SOUTH
20
20
10
10
500
600
700
800
900
1000
1100
1200
1300
1400
500
600
700
800
900
1000
1100
1200
1400
TRAJECTORY PATH BASED ON A VECTOR AVERAGE OF FIRST- AND SECOND-LEVEL WIND FIELDS
TRAJECTORY PATH BASED ON FIRST-LEVEL WIND FIELDS
AREA IN WHICH THE TRAJECTORY PATH CAN OCCUR IN THE AIRSHED MODEL SIMULATIONS

Figure 6-4. Comparison of trajectory paths based on two different wind patterns for 29 July 1977.

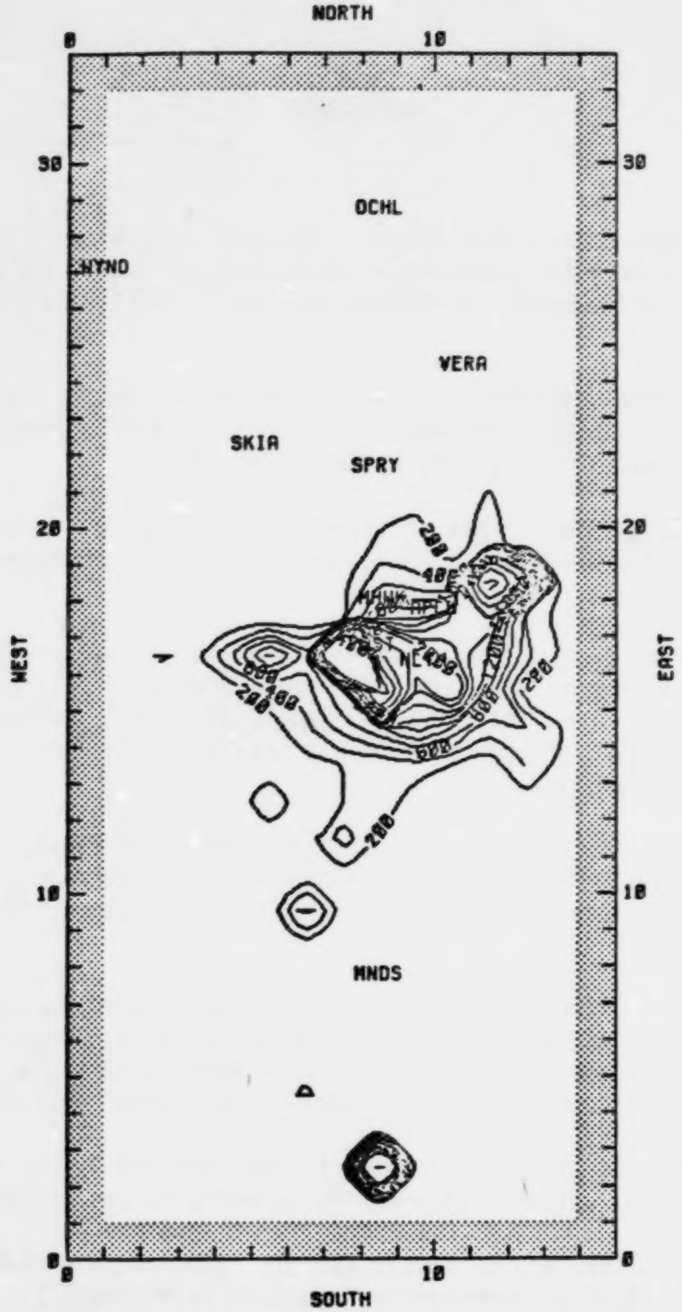

NORTH
0
10
30
20
10
0
OCHL
WYND
VERA
SKIA
SPRY
200
400
600
800
MNDS
WEST
EAST
SOUTH

Figure 6-5. Total ground-level emissions of hydrocarbons for the Tulsa region in kg/hr between the hours of 0800 and 0900 (CDT)

REFERENCES

Atkinson, R., and A. C. Lloyd (1980), "Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog," ERT No. P-A040, Environmental Research and Technology, Inc., Westlake Village, California.

Dodge, M. C. (1978), "Effect of Selected Parameters on Predictions of a Photochemical Model," EPA-600/3-77-048, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

EPA (1980), "Guideline for Use of City-Specific EKMA in Preparing Ozone SIPs," EPA-450/80-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Eaton, W. C., and F. E. Dimmock (1979), "Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma: Vol. II. Data Tabulation," EPA-450/4-79-008b, U.S. Environmental Protection Agency, Research Triangle Institute, Research Triangle Park, North Carolina.

Eaton, W. C., et al. (1979a), "Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma," EPA-450/4-79-008a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Eaton, W. C., et al. (1979b), "Study of the Nature of Ozone, Oxides of Nitrogen, and Nonmethane Hydrocarbons in Tulsa, Oklahoma--Vol. III, Data Analysis and Interpretation," EPA-450/4-79-008c, Research Triangle Institute, Research Triangle Park, North Carolina.

Engineering Science (1979), "Emission Inventories for Tulsa, Oklahoma for SAI Model Application," Engineering Science, McLean, Virginia.

Jeffries, H., D. Fox, and R. Kamens (1975), "Outdoor Smog Chamber Studies: Effect of Hydrocarbon Reduction on Nitrogen Dioxide," University of North Carolina, Chapel Hill, North Carolina.

Killus, J. P., and G. Z. Whitten (1981), "User's Guide to the Carbon-Bond Mechanism," SAI No. 75-81-EF81-90, Systems Applications, Inc., San Rafael, California.

Reid, L. E., S. D. Reynolds, and D. A. Latimer (1980), "Evaluation of Airshed Model Performance in Tulsa," Technical Memorandum No. 3, SAI No. 223-ES80-164, Systems Applications, Inc., San Rafael, California.

Reynolds, S. D., et al. (1979), "Photochemical Modeling of Transportation Control Strategies--Vol. I. Model Development, Performance Evaluation, and Strategy Assessment," prepared for the Federal Highway Administration, Office of Research, Washington, D.C.

Sellers (1965), Physical Climatology (University of Chicago Press, Chicago, Illinois).

Turner, D. B. (1969), "Workbook of Atmospheric Dispersion Estimates," AP-26, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Whitten, G. Z., H. Hogo, and R. G. Johnson (1981), "Application of the Empirical Kinetic Modeling Approach (EKMA) to Urban Areas," SAI No. 32R-EF80-139R, Systems Applications, Inc., San Rafael, California.

Whitten, G. Z., and H. Hogo (1981), "Comparative Applications of the EKMA in the Los Angeles Area," SAI No. 10R-EF80-73, Systems Applications, Inc., San Rafael, California.

Whitten, G. Z., and H. Hogo, (1978), "User's Manual for Kinetics Model and Ozone Isopleth Plotting Package," EPA-600/8-78-014a, Systems Applications, Inc., San Rafael, California.

Whitten, G. Z., J. P. Killus, and H. Hogo (1980), "Modeling of Simulated Photochemical Smog with Kinetic Mechanisms," EPA-600/3-80-028a, Systems Applications, Inc., San Rafael, California.

APPENDIX

DESCRIPTION OF INPUTS USED IN SAI AIRSHED MODEL SIMULATIONS

The following description of the inputs used in the SAI Airshed simulations are taken from Reid, Reynolds, and Oliver (1980). Many of the inputs derived for the less complicated models as discussed in the main part of the document are based on the inputs developed for the Airshed Model.

PREPARATION OF INITIAL AND BOUNDARY CONCENTRATION INPUTS

Three input files--AIRQUALITY, BOUNDARY, and TOPCONC--are required for the specification of initial and boundary conditions of all pollutants. The AIRQUALITY file specifies the concentrations of all species for all grid squares at the start time of the run. The data available for constructing this file are the monitoring data from the eight RTI sites and the two Tulsa City/County Health Department (TCCHD) stations, the hydrocarbon bag samples, and the aircraft flights. We used two methodologies for constructing gridded fields of initial conditions from the data--one for constructing the gridded ground-level concentrations, and one for extrapolating the concentrations aloft from the ground-level values.

To construct the initial and boundary concentration files, we examined the Tulsa air quality data base in order to characterize the levels and distribution of pollutants in the study area. Using this information and drawing on our previous experience in modeling other urban areas, we tried to identify pollutant concentrations and to establish reasonable methodologies for preparing these inputs. In cases in which there were little or no data specific to a modeling day, we chose to use average values rather than to develop a correlation between the parameter of interest and another parameter that was actually measured. This procedure enabled us to avoid estimating some parameter of interest on a day during which the conditions may have been quite different from those used in a correlation analysis.

The available NO_x and ozone data collected at the eight RTI monitoring stations were generally adequate to characterize the ground-level initial and boundary values for these pollutants. However, we had considerably fewer data with which to characterize the ground-level hydrocarbon initial and boundary conditions. To further complicate matters, pollutant concentrations aloft were measured on only one of the four days selected for model simulations. Of course, the range within which we could vary these hydrocarbon concentrations was limited by the uncertainty in the available data. The difficulty arises in separating the range of uncertainty from the range of real fluctuations. Although an average value for the latter can be considered to best represent the HC levels, a broad range of true uncertainty allows a more arbitrary choice of HC levels. The estimated HC levels are currently (as of this writing) being reevaluated; these original estimates involved HC/NO_x ratios (which varied over a wide range), actual HC measurements (which were extremely limited), and NO_x measurements (which varied over a wide range). As a result, considerable uncertainty exists in our specification of the initial and boundary concentration inputs, especially those for hydrocarbons.

Preparation of Gridded Ground-Level Initial Concentration Fields

We began the calculations at 0500 CDT as described earlier in section 3 of the main report. The hourly average concentrations observed at the monitoring sites for the hour ending at the starting time of the run were employed as the inputs to the interpolation routines that were used to calculate the gridded concentration fields. We used these measured values to estimate conditions at 0500 CDT rather than, say, the average of the 0400 to 0500 and 0500 to 0600 hourly average observations to avoid the possible influence that emissions subsequent to the simulation starting time would have on the measured values, and thus, the resulting initial concentration fields. In this study, we used an inverse distance weighting interpolation routine to construct the gridded surface fields. This relationship for the estimated concentration $\bar{c}_k$ in grid cell k can be written as follows:

$$\bar{c}_k = \frac{\sum_{i=1}^{n} c_{m,i}\, r_{ik}^{-1}}{\sum_{i=1}^{n} r_{ik}^{-1}} \quad ,$$

where $c_{m,i}$ is the measured concentration at monitor i, n is the total number of measured values, and r_{ik} is the distance from the monitor to the center of grid cell k.

In addition to the two TCCHD ozone monitors, eight RTI monitoring stations were used to estimate NO, NO_2, and O_3 ground-level concentrations. Since there is only one site (Liberty Mounds) in the southern third of the region, it was necessary to add "fictitious" monitoring stations in the southern end of the region to prevent the calculated concentrations in this area from being unduly influenced by the values observed at other stations to the north. In past modeling applications we have sometimes found it necessary to add stations in the corners of the modeling region and to give these stations background values that reflect the rural nature of the outlying portions of the grid. Otherwise, the mathematical routine for calculating gridded ground-level initial concentration values will extrapolate using data that are often collected in the more source-intensive portions of the grid. We added four "fictitious" stations in the southern third of the grid--one in each corner, one on the eastern edge, and one on the western edge, each about eight grid cells from the southern boundary. The pollutant concentrations at each of these stations were set to the background levels cited in table A-1, except for ozone, which was given a value of 0.04 ppm.

The amount of spatial variation in the early morning NO_x and O_3 monitoring data differed from day to day. For 21 July, the NO_x data ranged from 5 ppb at the rural stations to 70 ppb at the post office site. The post office observations exhibited the highest early morning NO_x concentrations. The NO_x measurements for 29 July were low with a range from 5 to 25 ppb. The third of August demonstrated the greatest variation in NO_x observations and the initial condition field reflects this, as can be seen in figure A-1(a). The data for 2 September again reflected the low values of NO_x observed on most days, with a high of 23 ppb. Most of the early morning ozone measurements for all the modeling days were around 30 ppb, with extreme values of 10 and 50 ppb. For this ozone to exist before dawn, the NO_x must have been predominantly in the form of NO_2 because of the rapid reaction of NO with ozone.

On any particular day, continuous hydrocarbon measurements were made at only two sites. Since these measurements did not provide sufficient data to specify the spatial variability of the ground-level hydrocarbon initial conditions, we found it necessary to tap other sources of hydrocarbon data. Additional available hydrocarbon data are the 0600 to 0900 CDT bag samples routinely taken at Liberty Mounds, health department, and the post office. Although these samples were taken during the morning rush hour, the data from Liberty Mounds should represent upwind concentrations, since there is little traffic in the area, and since few emissions sources exist near the site. The Okmulgee Refinery, which is about 20 to 25 km south of the Liberty Mounds monitoring station, is the only potentially significant nearby emissions source. To assess the impact of the refinery, we used the formulas given by Turner (1969) for calculating

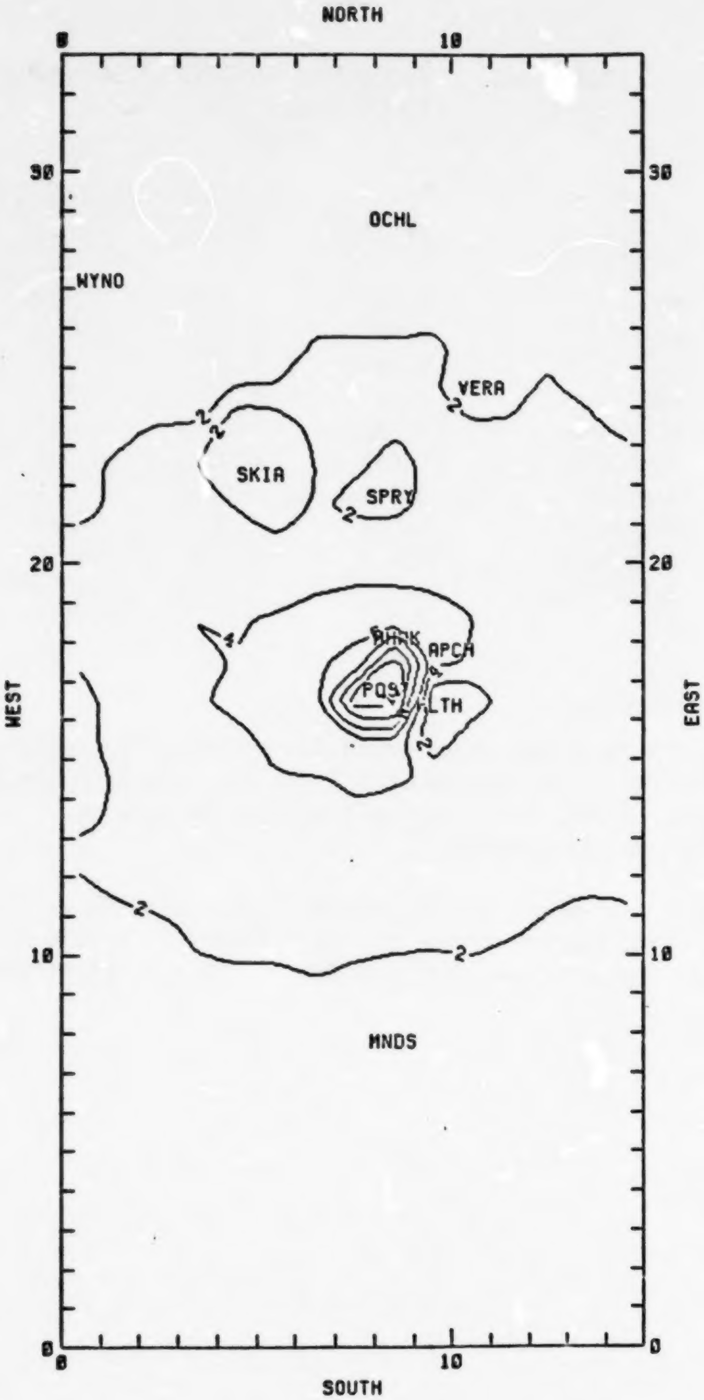
TABLE A-1. BACKGROUND CONCENTRATIONS USED IN THE TULSA SIMULATIONS (ppm)

Species	Background Concentrations			
	21 July	29 July	3 Aug.	2 Sept.
NO	0.0005	0.0005	0.0005	0.0005
NO_2	0.002	0.002	0.002	0.002
O_3	0.06	0.08*	0.06	0.05†
NMOC	0.24	0.20	0.21	0.17
Ethylene	0.0058	0.0049	0.0051	0.0041
Paraffins	0.065	0.053	0.056	0.046
Olefins	0.0014	0.0012	0.0013	0.0010
Aromatics	0.012	0.009	0.010	0.008
Carbonyls	0.012	0.009	0.010	0.008
Benzaldehyde	0.00001	0.00001	0.00001	0.00001
CO	0.1	0.1	0.1	0.1

---

* For 29 July, the ozone boundary concentrations on the sides of the modeling region varied with location. The boundary values on the north, south, east, and west boundaries were 0.07, 0.08, 0.06, and 0.08 ppm, respectively.

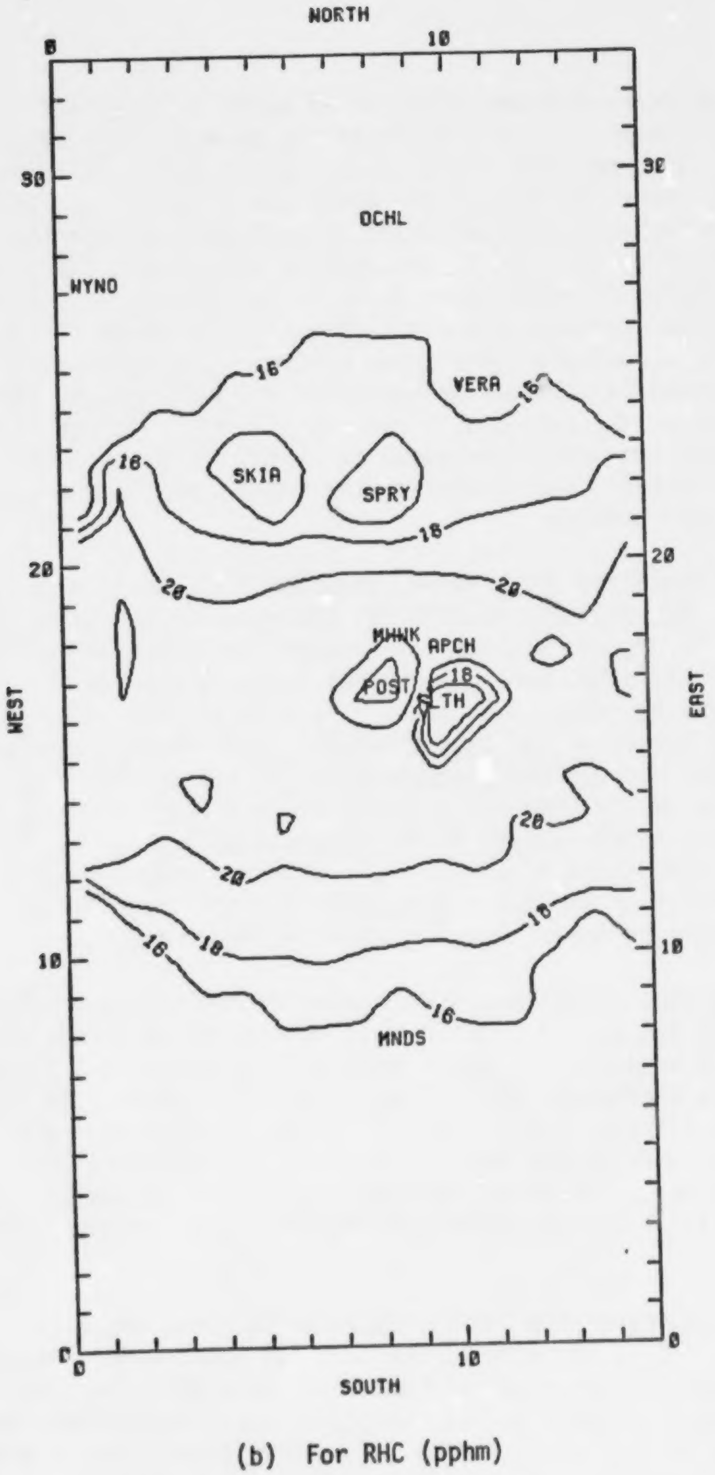
† For 2 September, the O_3 boundary concentration at the top of the modeling region varied in time: From 400 to 1100 CST, it was set at 0.07 ppm and from 1100 to 2100 CST, it was set at 0.05 ppm.


NORTH
SOUTH
WEST
EAST
0
10
20
30
OCHL
WYNO
VERA
SKIA
SPRY
AHHK
APCH
POST
LTH
MNDS
2
4

(a) For NO_x (pphm)

Figure A-1. Initial conditions in the ground-level grid cells on 3 August 1977 (isopleths in increments of 2 pphm).

49r 81 18



(b) For RHC (pphm)

Figure A-1.(concluded).

pollutant concentrations downwind of point sources, and assuming D (neutral) stability, we calculated the expected hydrocarbon concentrations at Liberty Mounds that could be attributed to the refinery. For the case in which the centerline of the plume was directly over the monitoring site, the expected concentration is 0.08 ppm, and for the case in which the centerline was 2 km to the east or west of the site, the expected concentration is 0.015 ppm. It is unlikely that the refinery plume was directly in line with the monitoring site for three hours. Furthermore, since the nonmethane hydrocarbon concentration measured at Liberty Mounds on the modeling days was between 0.17 and 0.24 ppm, it appears that the influence of the refinery is not significant. Therefore, we used the nonmethane hydrocarbon measured at Liberty Mounds between 0600 and 0900 CDT as the basis for estimating the background concentrations of the carbon-bond species.

In preparing the gridded hydrocarbon ground-level initial concentration fields, the 0600 to 0900 CDT nonmethane hydrocarbon value measured at Liberty Mounds was assumed to represent the hydrocarbon level that would exist at the other monitoring sites unless a continuous hydrocarbon instrument happened to be located at a particular site, in which case we used the larger of the 0600 to 0900 Liberty Mounds value or the actual nonmethane hydrocarbon concentration for the hour ending at 0500 CDT. This methodology produced a fairly uniform initial concentration field, except for higher values in the downtown area. Available measurements suggest that there is a relatively high background concentration of hydrocarbons in the Tulsa area, possibly attributable to natural sources, oil production activities, or other upwind anthropogenic sources.

The NMOC values assumed to exist at monitoring locations and used to construct the ground-level initial concentration fields when data were not otherwise available at these locations are summarized in table A-1, which lists the background NMOC values. The only instance in which the continuous NMOC differed significantly from the Liberty Mounds values occurred on 3 August, when at the post office site, a NMOC concentration of 0.60 ppm was observed. The effect of this measurement on the calculated ground-level initial concentrations of reactive hydrocarbons is shown in figure A-1(b).

Since there were limited data for CO, SO_2, and total suspended particulate (TSP), we chose to use only low background concentrations for these species. Of these contaminants, only CO is included because it is one of the reactants in the chemical kinetic mechanism. Because the chemistry is not too sensitive to CO concentrations, use of the natural background value of 0.1 ppm for initial conditions seemed a reasonable basis for establishing this model input. For the 2 September simulation, the model was employed to calculate aerosol concentrations, and thus it was necessary to have initial conditions of SO_2 and aerosols. For SO_2 we used a constant 0.01 ppm and a 0.0 $\mu g/m^3$ aerosol concentration.

The chemistry package in the SAI Airshed Model contains five different hydrocarbon species that are referred to as the Carbon-Bond species:

> ETH
> PAR
> OLE
> CARB
> ARO.

The available nonmethane hydrocarbon data must be split among the Carbon-Bond species. The bag sample data collected in Tulsa were used to estimate the splits for each species according to the factors presented in table A-2. At the start of the simulation period when the mixing layer is relatively shallow, a large portion of the modeling region is located above the inversion base. As a result, we decided to use the bag samples collected by the aircraft to estimate the hydrocarbon splits. In this study, we averaged all the valid data and used the same splits for all the runs. The resulting splits employed in estimating initial and boundary conditions are summarized in table A-3. Averaged data rather than day-specific data were used to avoid placing too much emphasis on a single-composition determination.

The gas chromatographic (GC) measurements used to analyze the hydrocarbons from the bag samples did not report carbonyls, so it was necessary to estimate the splits for these species from other sources. In past model applications we assumed about 5 percent of the initial NMOC to be carbonyls, and thus we have employed this value in the Tulsa simulations.

The carbonyl assumption is based on our work in simulating smog chamber experiments (J. P. Killus, private communication, 1979), the hydrocarbon fraction of the predictions at the end of simulations for other cities, and the carbonyl fraction in the emissions inventory for Tulsa. To test the reasonableness of the assumption, we calculated the carbonyl fraction from the model results for the last hour (2000 to 2100 CDT) of the 21 July simulation. Using the hydrocarbon predictions at the 10 stations, we found that the average carbonyl fraction was 0.06 with a range between 0.02 and 0.14. In addition, there was a positive correlation with distance from downtown Tulsa. Therefore, a carbonyl fraction of 0.05 seems quite reasonable. The justification for using carbonyl splits from the end of a simulation day lies in the assumption that the percentage split does not vary significantly from one day to the next. Also involved is the assumption that the chemical mechanism that generates reactive intermediates such as the carbonyls is representative of the actual atmospheric chemistry.

TABLE A-2. SPLITTING FACTORS FOR THE HYDROCARBON SPECIES MEASURED IN THE TULSA STUDY

(ppm/ppmC of HC species)

	Carbon-Bond Species Equivalents			
Hydrocarbon Species	PAR	OLE[*]	ARO[†]	ETH[*]
Ethane	--	--	--	--
Ethylene	--	--	--	0.5
Propane	0.5[§]	--	--	--
Acetylene	--	--	--	--
Isobutane	1.0	--	--	--
n-Butane	1.0	--	--	--
Propylene	0.33	0.33	--	--
Isopentane	1.0	--	--	--
n-Pentane and cyclopentane	1.0	--	--	--
Trans-2-pentene + isoprene	0.6	0.2	--	--
2,2-Dimethylbutane	1.0	--	--	--
Methylpentane	1.0	--	--	--
1-Hexene	0.67	0.17	--	--
Hexane	1.0	--	--	--
Dimethylpentane	1.0	--	--	--
Methylhexane	1.0	--	--	--
2,2,4-Trimethylpentane	1.0	--	--	--
n-Heptane	1.0	--	--	--
Methylcyclohexane	1.0	--	--	--
2,3,4-Trimethylpentane	1.0	--	--	--
Methylheptane	1.0	--	--	--
n-Octane	1.0	--	--	--
n-Nonane	1.0	--	--	--
n-Decane	1.0	--	--	--
n-Undecane	1.0	--	--	--
n-Dodecane	1.0	--	--	--
Benzene	--	--	--	--
Toluene	0.14	--	0.14	--
Ethylbenzene	0.25	--	0.13	--
Xylene	0.25	--	0.13	--
n-Propylbenzene	0.33	--	0.11	--
Ethyltoluene	0.33	--	0.11	--
Trimethylbenzene	0.33	--	0.11	--
Butylbenzene	0.40	--	0.10	--

---

[*] Each olefin and ethylene contain two carbon atoms.

[†] Each aromatic contains six carbon atoms.

[§] A factor of 0.5, rather than 1, is used for propane to account for the lower reactivity of this compound relative to that of the other species that contain single-bonded carbon atoms.

TABLE A-3. HYDROCARBON SPLITS USED IN THE TULSA SIMULATIONS

Carbon-Bond Type	Hydrocarbon Splits* (fraction of NMOC by Carbon-Bond type)	Standard Deviation
Ethylene	0.024	0.026
Paraffins	0.268	0.138
Olefins	0.006	0.009
Aromatics	0.05	0.036
Carbonyls	0.05	--
Benzaldehyde	0.00001	--

---

* Ethane, acetylene, and benzene, as well as 50 percent of the propane, were considered unreactive in our analysis of the available ambient hydrocarbon composition data.

Preparation of Aloft Initial Concentration Fields

Although the monitoring data provide the primary means for estimating ground-level initial conditions, they give no direct information about the vertical profile of pollutant concentrations. The aircraft flights provide the only source of air quality data aloft. However, only one of the modeling days corresponds to a flight day; thus, the aircraft data can be used only as a guide for the other three days. When the mixing depth is rising rapidly, observations at upwind monitors can also give an indication of the concentrations aloft. The ozone data aloft, measured during morning aircraft flights, indicate a consistent pattern. Of the five morning flights conducted during southerly transport conditions, all but one (17 September) measured a fairly constant ozone concentration of between 0.06 and 0.08 ppm. As shown in table A-4, the average ozone aloft measured during the morning spiral over Liberty Mounds agrees quite well with the late morning (1000 to 1200 CST) ground-level value reported at this site. In specifying the ozone levels aloft, we considered the late morning ozone measurements reported for those stations that were not influenced by emissions from the Tulsa city area. The aloft measurements of NO_x were generally all below 0.01 ppm, corresponding to the observations at the upwind stations.

Because of the paucity of aloft data on three of the modeling days, we used a fairly simple vertical profile for initial conditions. The cells within the mixed layer were given the calculated surface concentration, and the cells above the mixing height were set at the aloft values estimated from the aircraft flights (when available) and the observations at upwind stations. For the 21 July, 29 July, and 3 August simulations, we set the initial NO and NO_2 concentrations above the mixed layer to 0.5 and 2 ppb, respectively. Ozone concentrations above the mixed layer were set to 0.06 ppm for the 21 July and 3 August simulations and to 0.08 ppm for the 29 July run.

For the 2 September 1977 simulation, day-specific data were available from the aircraft flights for specifying pollutant concentrations aloft. Figure A-2 shows the data collected during the morning spiral over Liberty Mounds on 2 September. The vertical profiles of NO and NO_x are essentially constant and at near-zero levels. The ozone profile shows more variation, with the concentration near the ground at about 0.05 ppm, rising to 0.08 ppm at approximately 600 m above the ground and then decreasing to between 0.05 and 0.06 ppm.

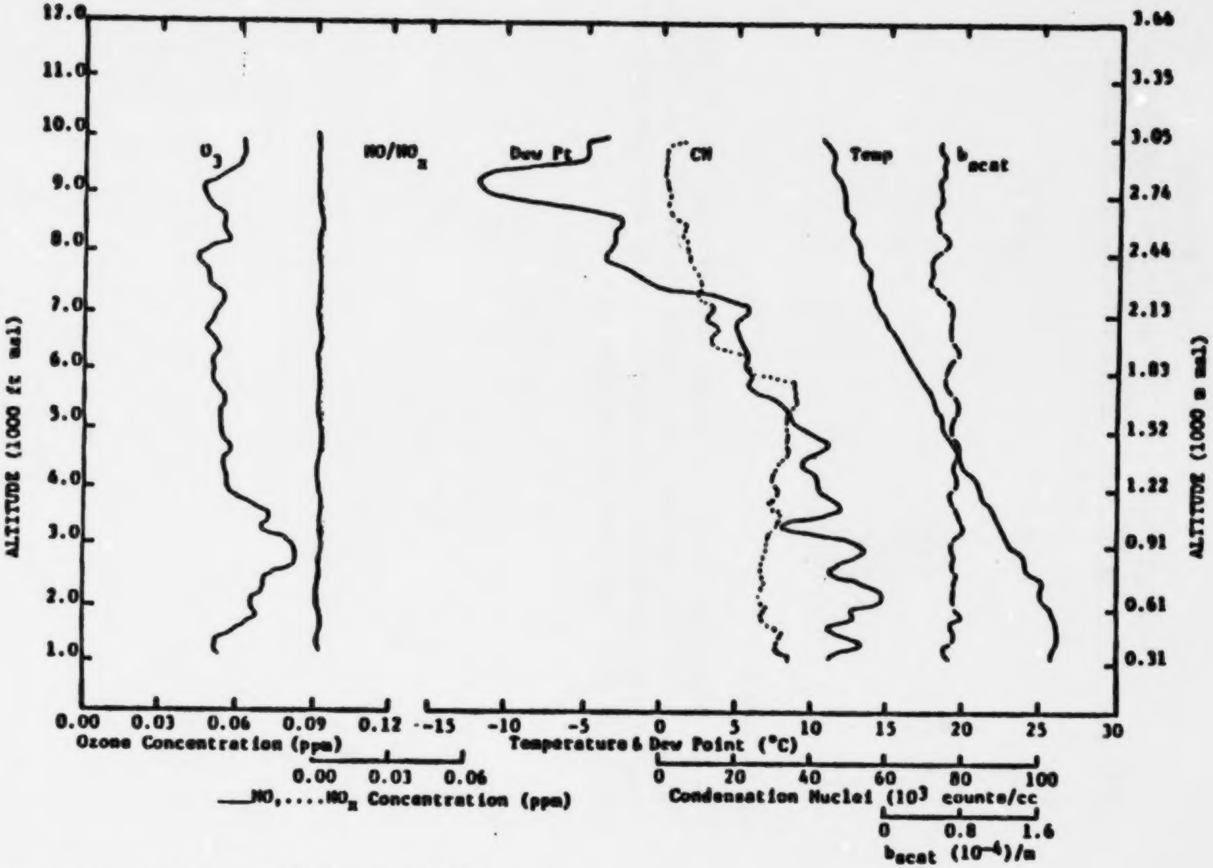
We examined various methods for estimating the background concentrations of hydrocarbons which were employed to characterize hydrocarbon

TABLE A-4. COMPARISON OF AIRBORNE AND GROUND-LEVEL OZONE CONCENTRATIONS AT LIBERTY MOUNDS IN 1977 (ppm)

Date	Average Ozone Aloft	Late Morning Ground-Level Ozone Between 1000 and 1200 CST
August		
26	0.06	0.053
September		
2	0.06	0.055
3	0.07	0.065
16	0.07	0.063*
17	0.05	0.051

---

* On 16 September 1977, the skies were overcast until 1100 CST, after which the ambient temperature increased significantly. Therefore, the ozone concentration cited here was measured between 1100 and 1300 CST on that day.



Source: Eaton and Dimmock (1979).

Figure A-2. Data collected during a morning vertical spiral over Liberty Mounds on 2 September 1977 (Tulsa Flight T09).

concentrations aloft. The data from Liberty Mounds and Wynona were more representative of background concentrations than were the data taken in the city of Tulsa. Furthermore, since the winds were primarily from the south on the modeling days, and since more data were obtained at Liberty Mounds than at Wynona, we selected the Liberty Mounds data. Since a large portion of the modeling region at the start of a simulation is situated above the mixed layer, we chose to analyze the aircraft bag sample data in order to determine the characteristic composition of the background hydrocarbons. Using these average composition figures, the 0600 to 0900 Liberty Mounds NMOC measurements, and assuming a flat initial hydrocarbon vertical concentration profile, we were able to establish the complete initial hydrocarbon concentration fields input to the model.* A summary of these hydrocarbon levels is provided in table A-1.

Preparation of Boundary Concentration Fields

The boundary concentrations on the sides and top of the modeling region for the 21 July and 3 August simulations were set equal to the initial concentrations above the mixed layer. Thus, the boundary values were constant both spatially and temporally. For the 29 July run, different values of the ozone concentration were specified for each boundary. Wind and air quality data reported at the Wynona and Ochelata stations suggest that different air masses influenced these two stations. Based on the observed ozone concentrations at times of inflow to the modeling region, we set the ozone values on the western, northern, and eastern boundaries to 0.08, 0.07, and 0.06 ppm, respectively. Ozone concentrations on the southern boundary were set to 0.08 ppm based on the Liberty Mounds observations and the ozone concentrations specified aloft. Hydrocarbon boundary concentrations were set to the background values cited in table A-1.

On 2 September, the ozone measurements made by the aircraft were used to specify the boundary concentrations at the top of the region. As the height of the region for this simulation increased, the top of the grid passed through the ozone gradient noted in the previous section. To account for the variation in the ozone aloft we varied the ozone concentration in the TOPCONC file. Ozone was set to 0.07 ppm for the hours before 1200 CDT and to 0.05 ppm for later hours. This variation produced the added effect of setting the ozone concentration above the inversion base to 0.07 ppm in the initial conditions. The initial conditions above the mixing height were similarly affected. The morning horizontal aircraft traverses on 2 September and the Liberty Mounds surface observations suggest that the boundary concentrations for NO and NO_2 at the edges of the region can be set to 0.5 and 2 ppb, respectively.

---

* Subsequent analysis has indicated that this procedure for estimating hydrocarbons aloft may lead to an overestimation of paraffin and aromatic concentration levels.

PREPARATION OF METEOROLOGICAL INPUTS

The meteorological inputs to the SAI Airshed Model determine the transport characteristics and rate of mixing of the pollutant cloud. Meteorological factors often account for the fact that the NAAQS is violated on some days and not on others, even when the emissions patterns are similar. Therefore, the windfield and the hourly mixing depths are important inputs to the airshed model. At the same time, upper air meteorological data were collected in Tulsa only on a limited number of special study days. As a result, the three-dimensional structure of the wind field was one of the most difficult model inputs to specify. We note that the initial and boundary concentrations aloft were equally difficult to estimate, again because of a dearth of measurements aloft on three of the days of particular interest in this study.

The Wind Field

In addition to the airport site, which collected instantaneous values every hour, four RTI sites measured hourly average wind speed and direction. As with the construction of the initial conditions, the three-dimensional windfield was calculated in two steps: first, the surface field was prepared, then the upper-level windfields. The surface windfield was developed using the ground-level measurements plus synthesized data and an interpolation routine that weights the observations by the inverse of the distance from the grid square. Mathematically, this relationship can be written

$$\bar{u}_k = \frac{\sum_{i=1}^{n} u_i r_{ik}^{-1}}{\sum_{i=1}^{n} r_{ik}^{-1}} ,$$

$$\bar{v}_k = \frac{\sum_{i=1}^{n} v_i r_{ik}^{-1}}{\sum_{i=1}^{n} r_{ik}^{-1}} ,$$

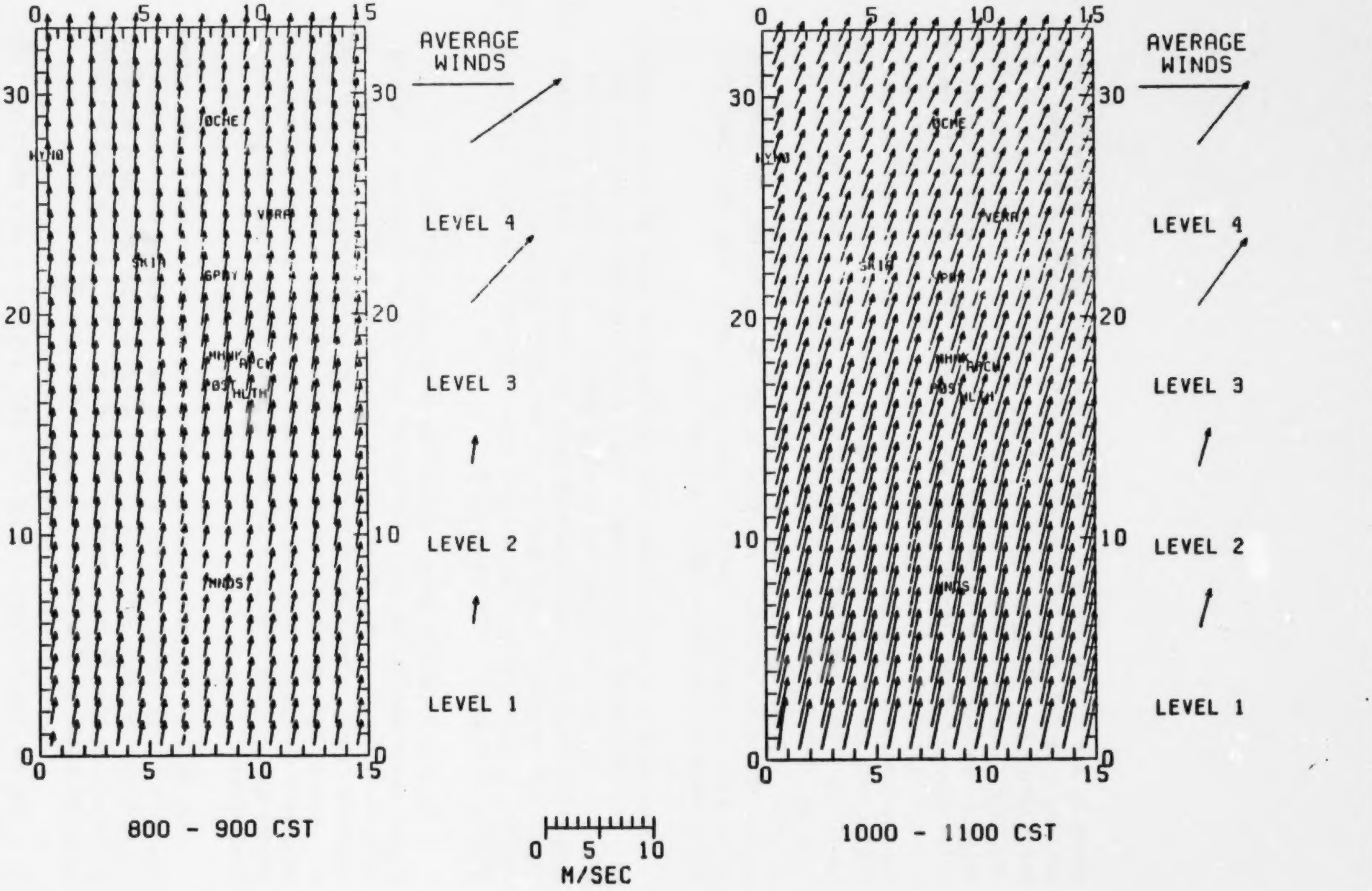
where $\bar{u}_k$ and $\bar{v}_k$ are the calculated horizontal velocity components for grid cell k, u_i and v_i are the measured velocity components at station i, n is the number of wind measurements, and r_{ik} is the distance between monitoring site i and grid cell k. A smoothing algorithm, which replaces each velocity component estimated above by the average velocity component calculated over the block of nine surrounding cells, was used to smooth the calculated wind field to eliminate any discontinuities introduced by the interpolation procedure. Finally, we calculated the average measured wind speed and the average computed wind speed over the modeling region resulting from the preceding calculations. The wind speed in each grid cell was then scaled by the ratio of the average measured speed to the average computed speed. This last operation was implemented since the vector averaging processes embedded in the interpolation and smoothing steps yield a computed flow field with wind speeds that are lower than those exhibited by the original observations.

The wind field calculated from the reported data only was compared with the pollutant observations. The comparison was carried out both visually and by exercising the airshed model. It was clear from the comparison that some modifications were necessary for most of the modeling days. For instance, there were hours for which the wind observations suggest a more complex flow pattern than that which could be calculated by simply interpolating the observations.

Two modifications were made to the wind data--adjustments to the actual measurements and the addition of synthesized data for locations relatively far from any observation sites. These modifications were subjectively based on wind observations, air quality observations, and synoptic weather maps obtained from the National Weather Service. Synthesized data were developed using available information to draw streamlines and adding synthesized wind data so that the calculated field follows the streamlines.

On 21 July 1977 the winds were from the south for almost the entire day with little variation from site to site. Since no problems were encountered in calculating the surface windfield for this day, no modifications were made to the reported wind data. The surface wind field for selected hours on this day are shown in figure A-3(a).

The air quality data for 29 July 1977 suggest a very sharp spatial gradient in ozone concentrations across the city. The monitor at Apache

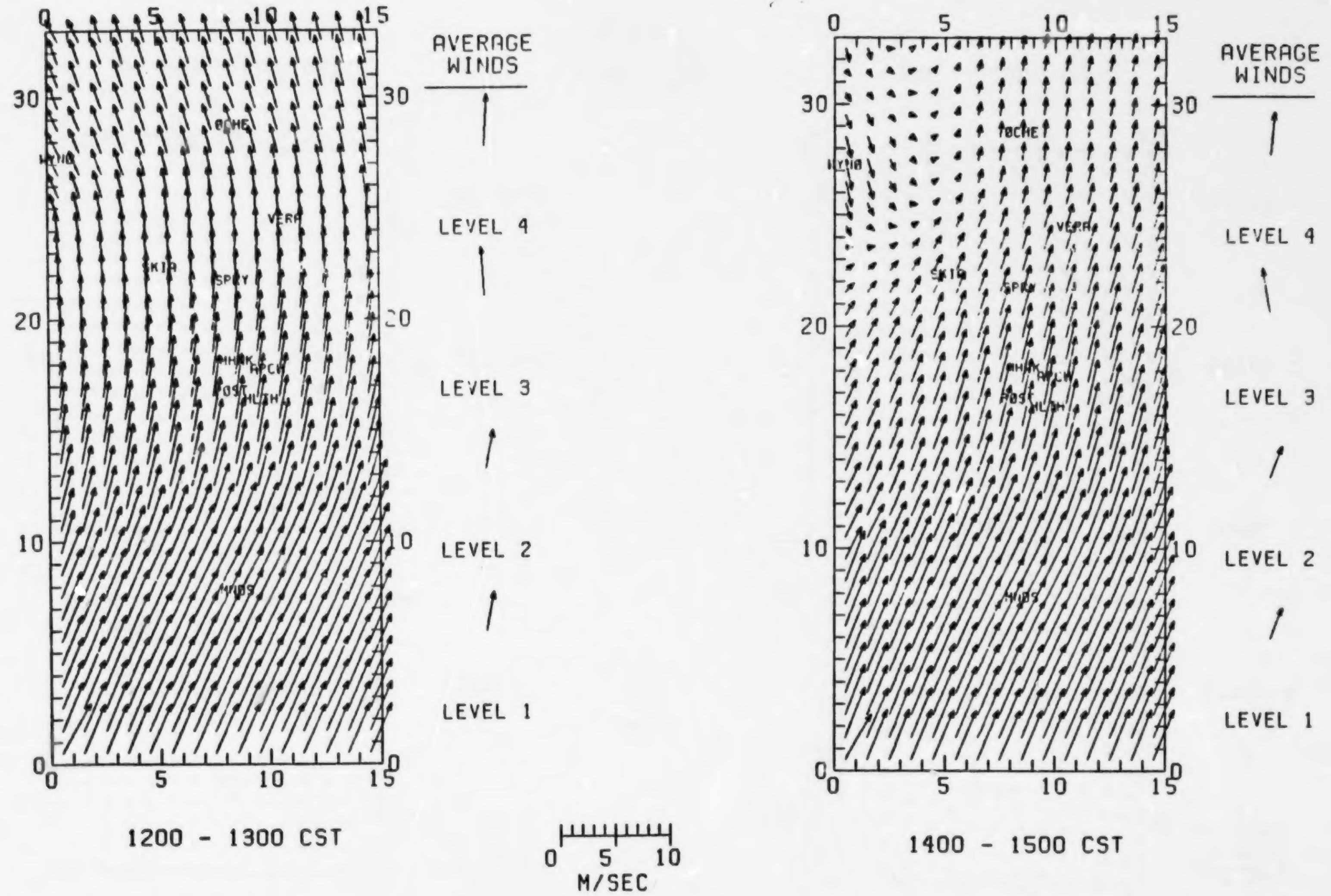


(a) 21 July 1977

Figure A-3. Calculated Wind Fields for Selected Hours for the Tulsa Region.

49r 81 18

49r 81 18

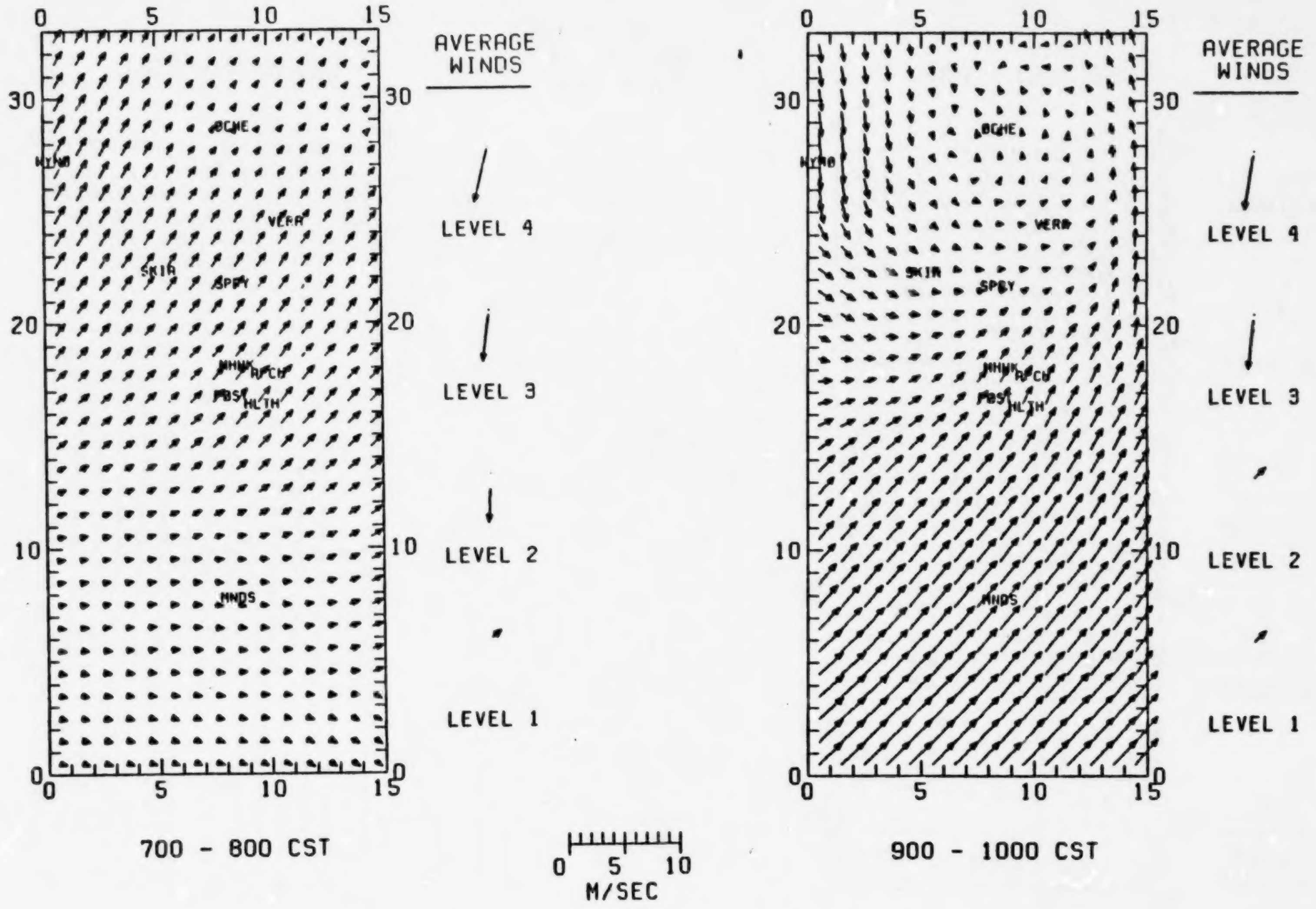


1200 - 1300 CST

1400 - 1500 CST

(a) (Concluded)

Figure A-3 (Continued).

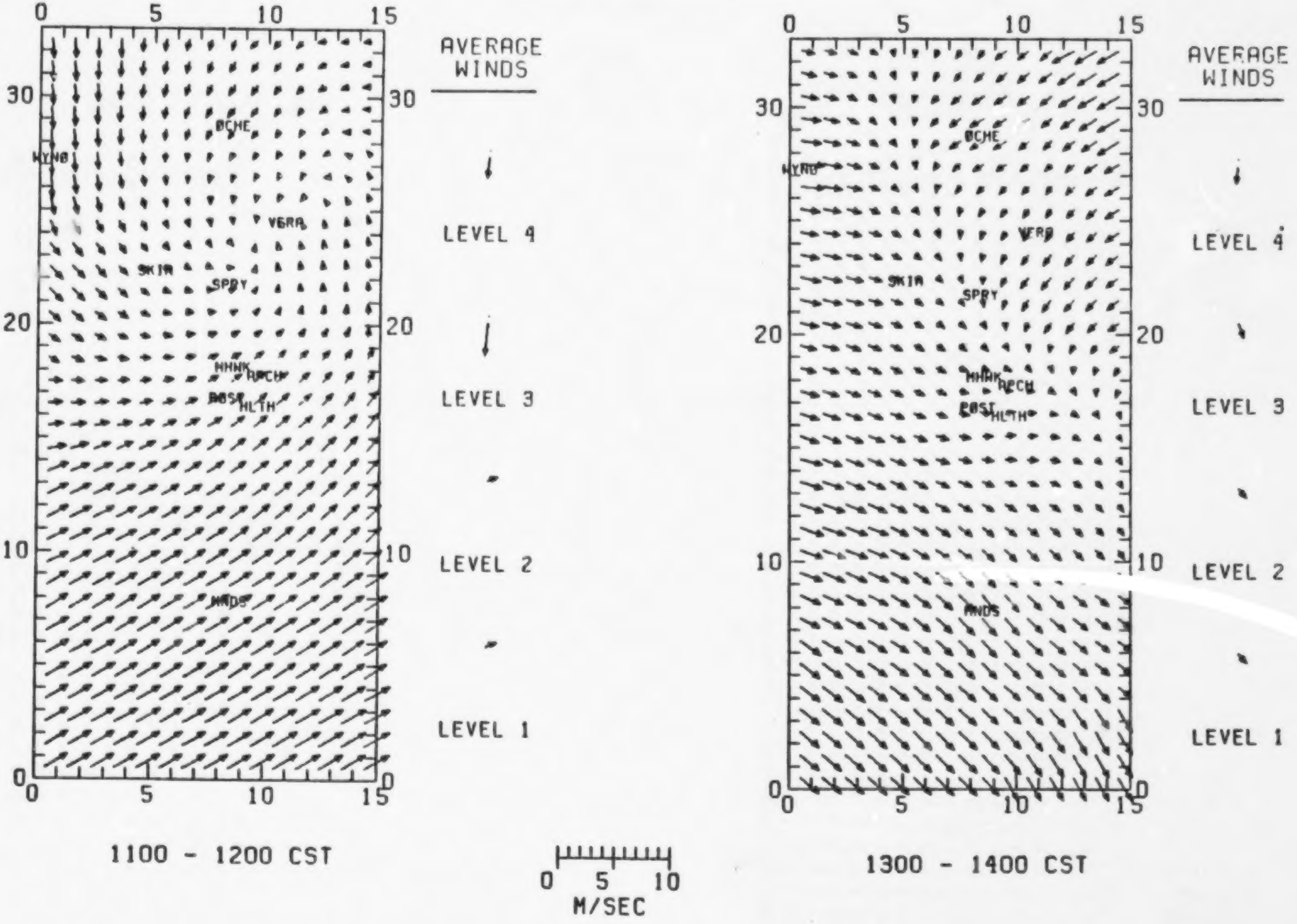


700 - 800 CST

900 - 1000 CST

(b) 29 July 1977

Figure A-3 (Continued).

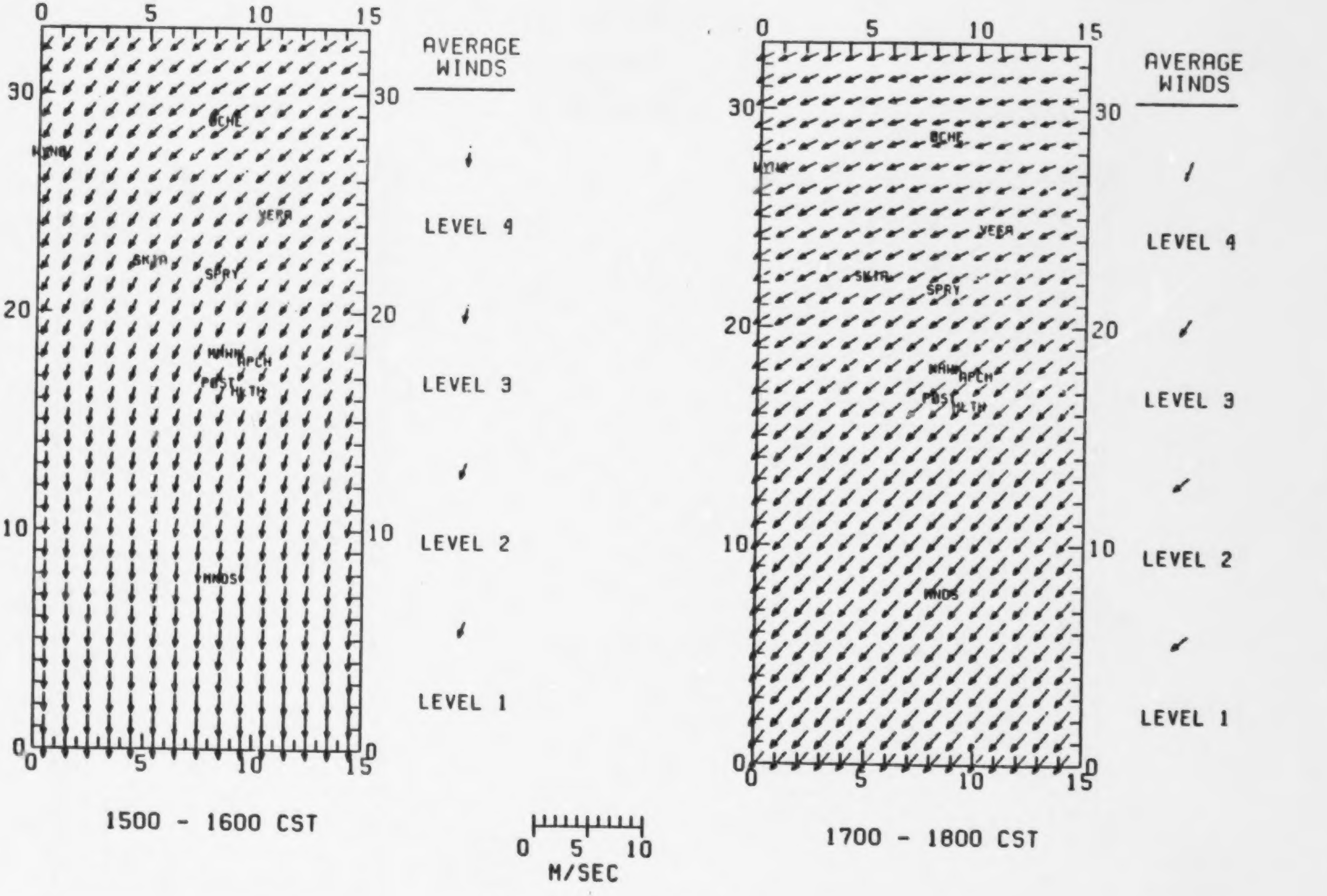


1100 - 1200 CST

1300 - 1400 CST

(b) (Continued)

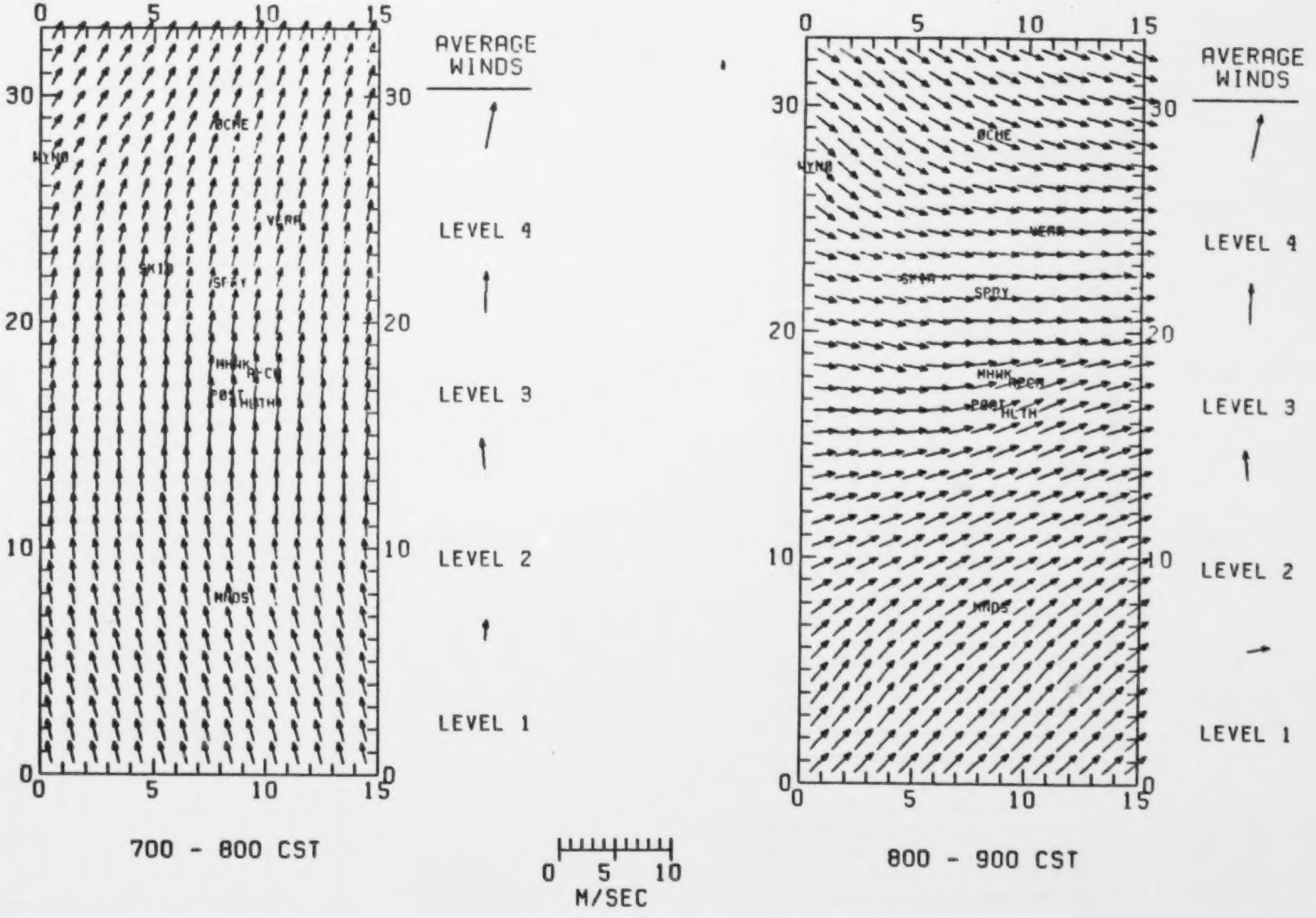
Figure A-3 (Continued).



(b) (Concluded)

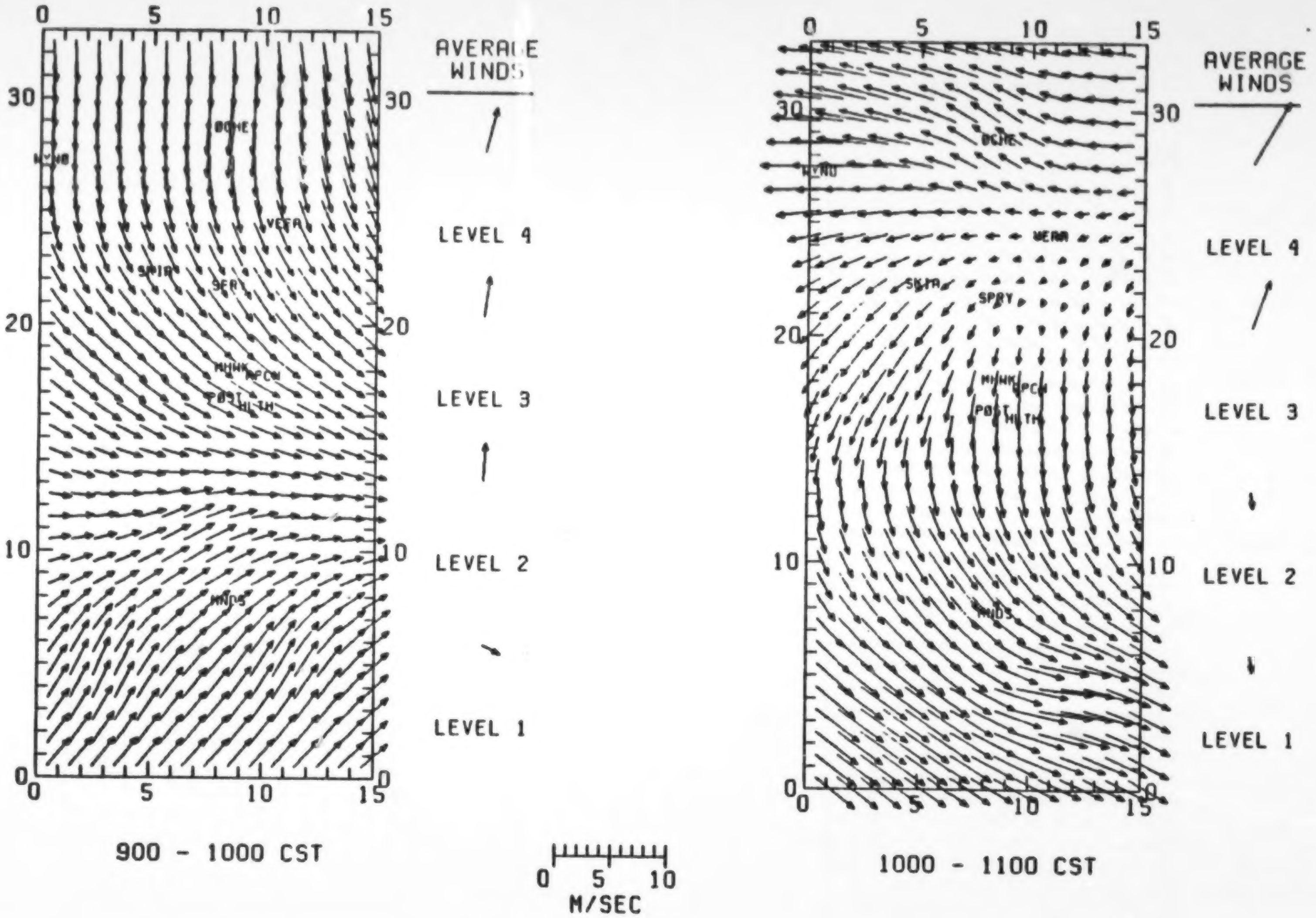
Figure A-3 (Continued).

49r 81 18



(c) 3 August 1977

Figure A-3 (Continued).

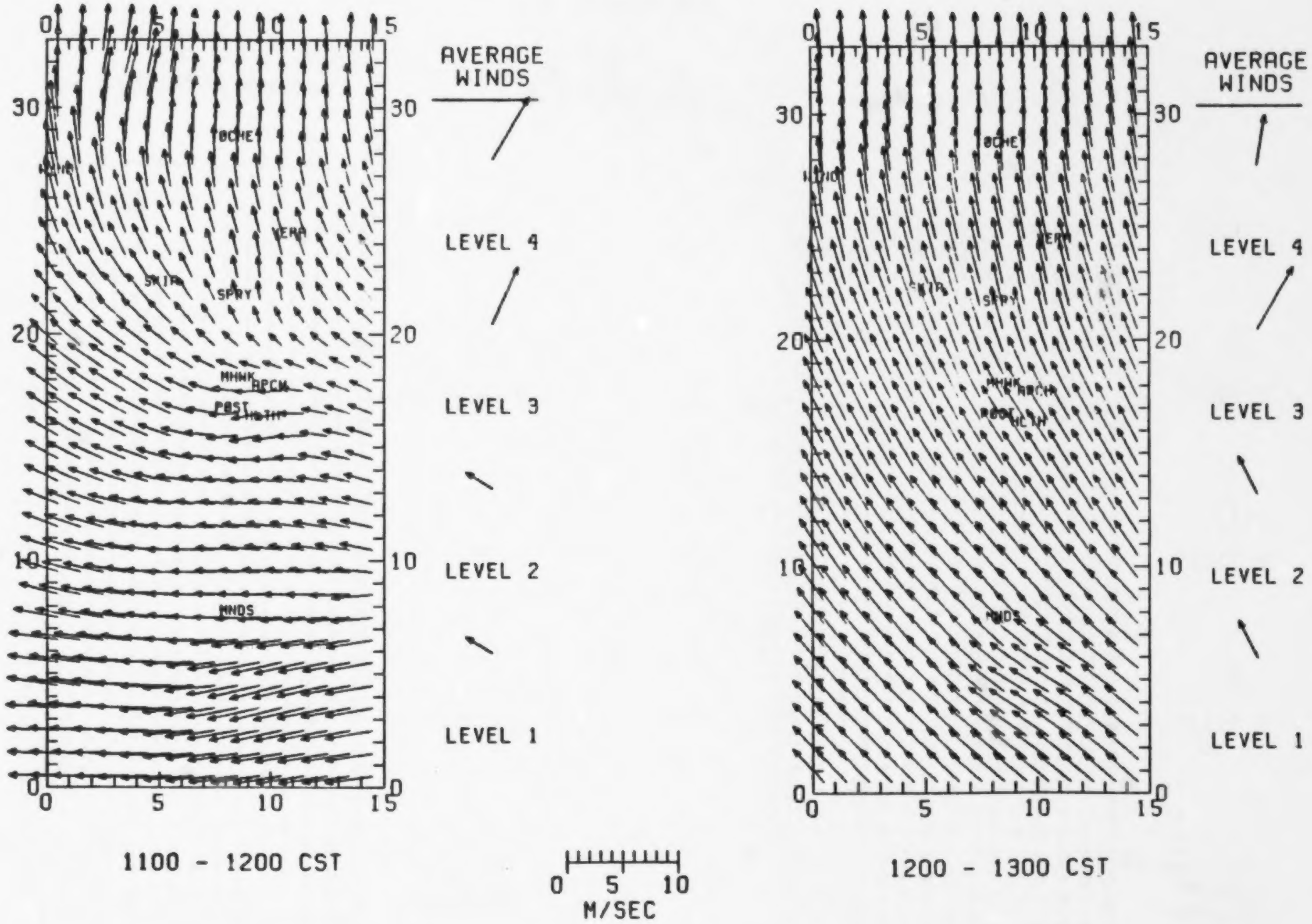


900 - 1000 CST

1000 - 1100 CST

(c) (Continued)

Figure A-3 (Continued).



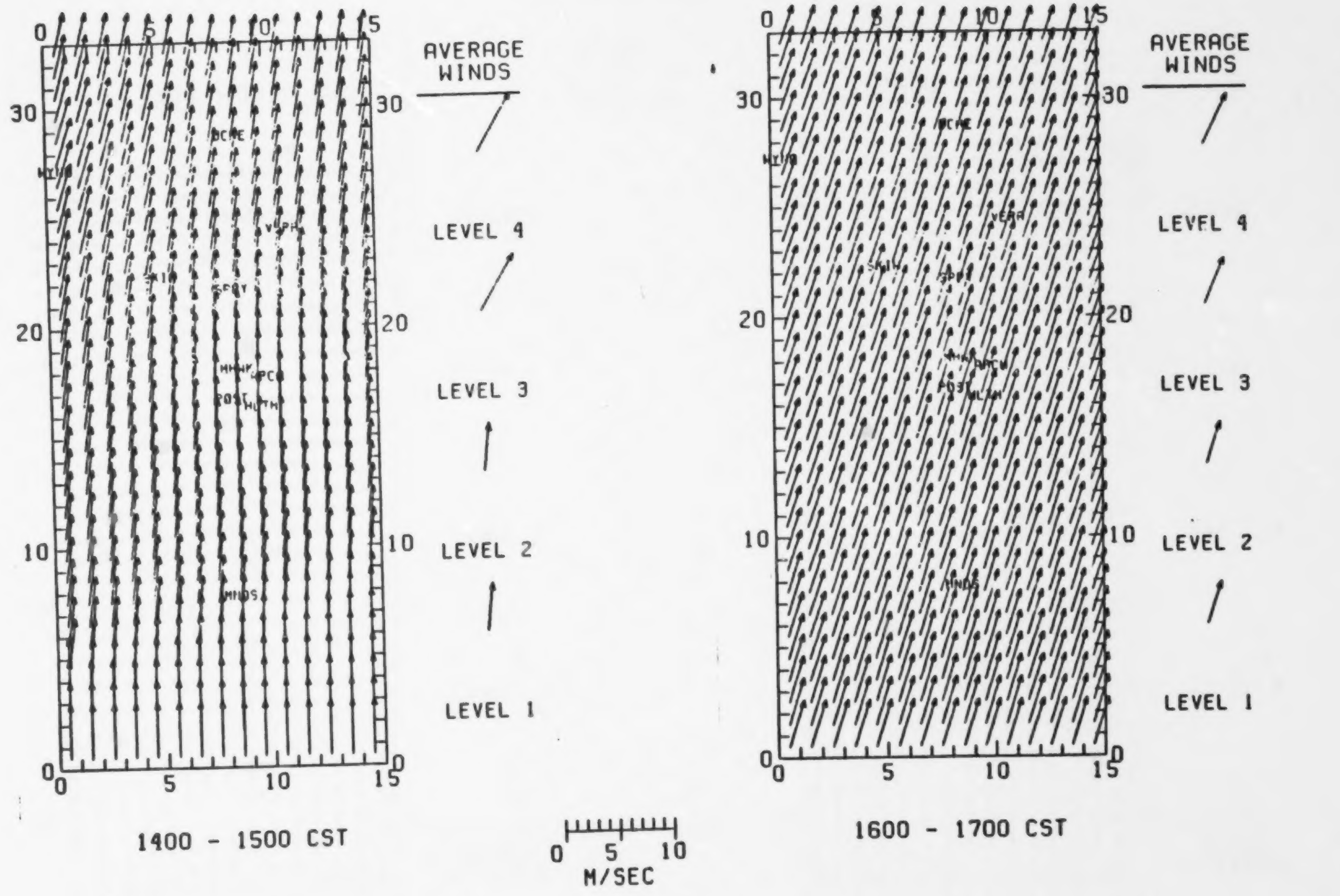
1100 - 1200 CST

1200 - 1300 CST

(c) (Continued)

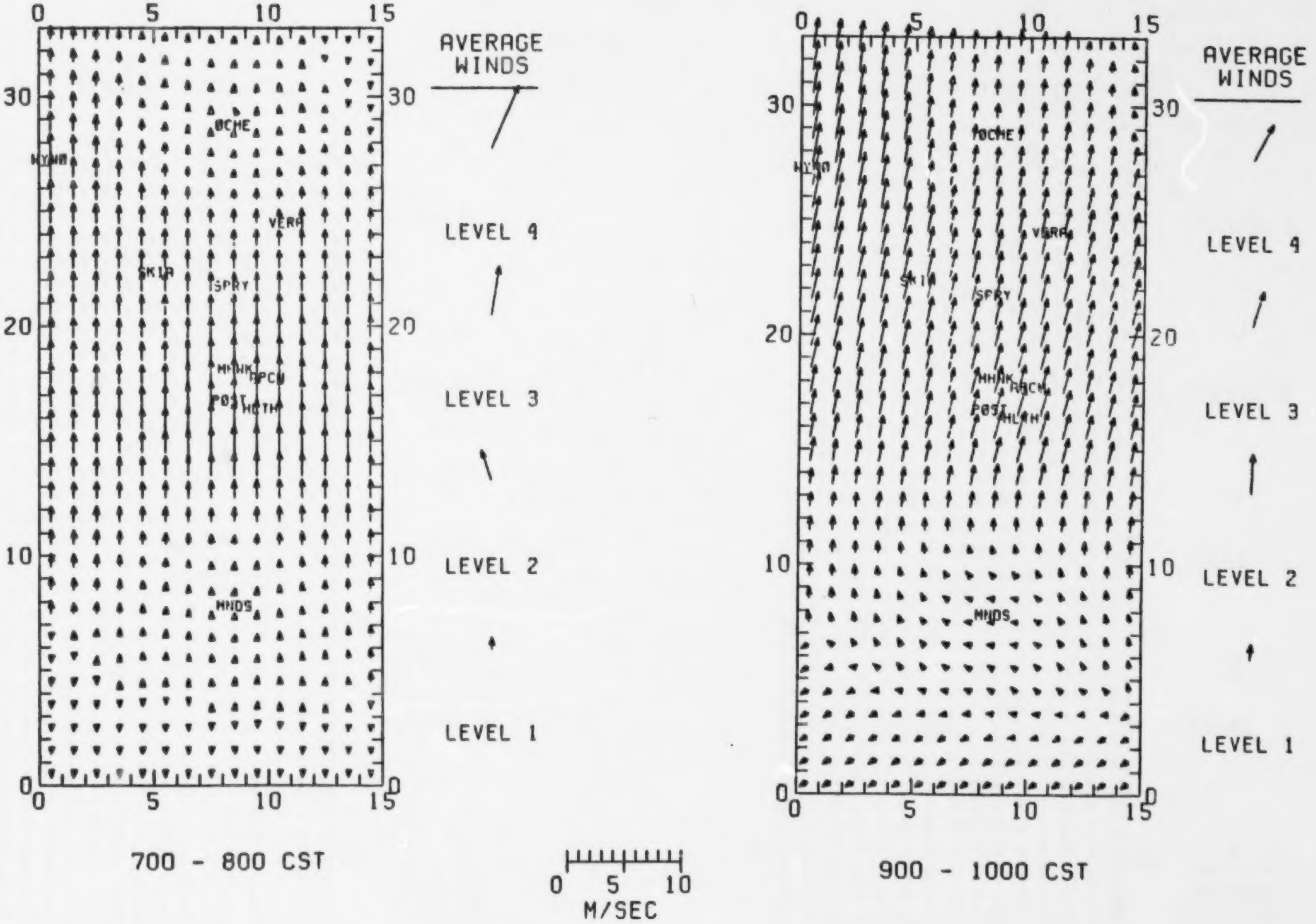
Figure A-3 (Continued).

49r 81 18



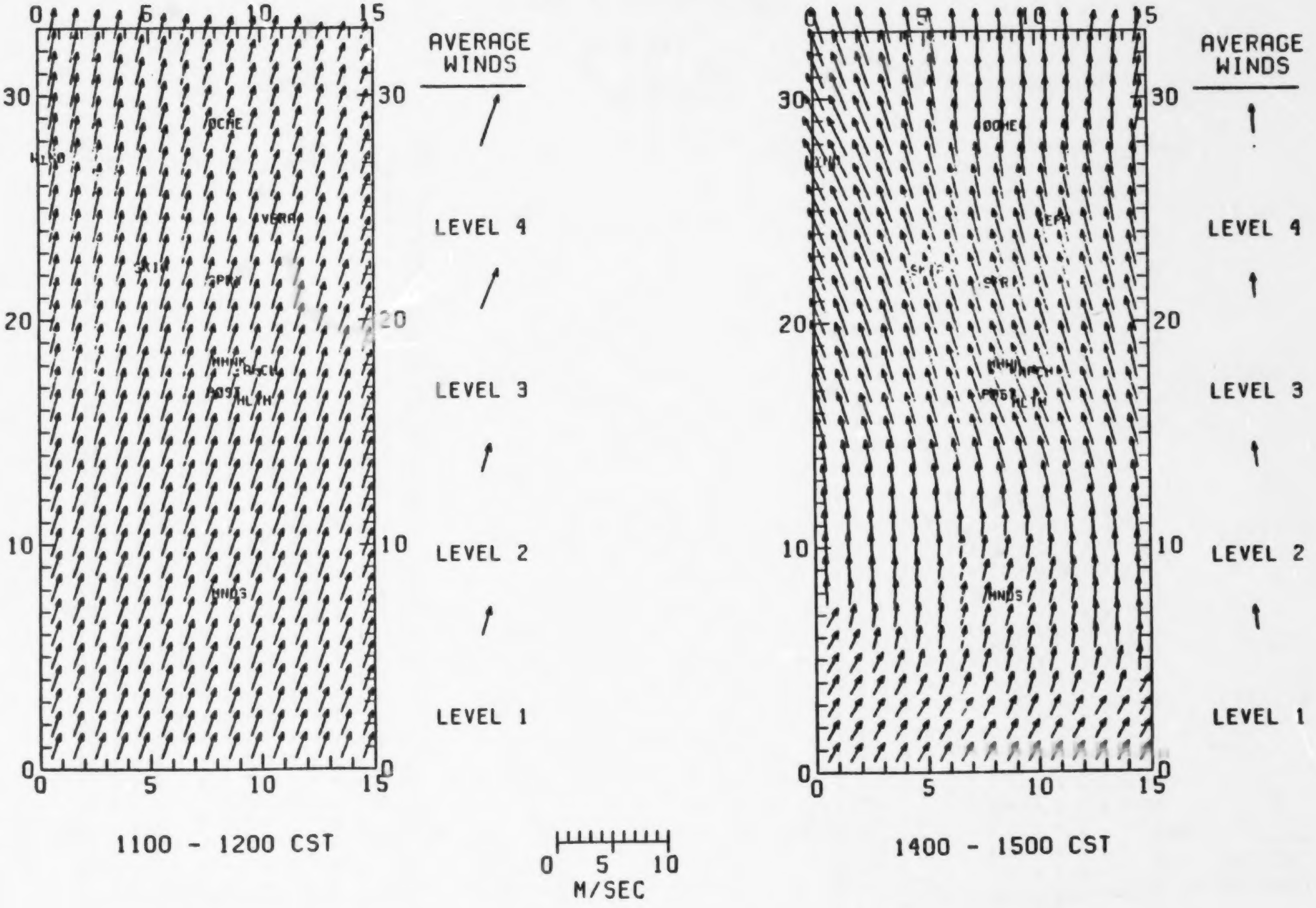
(c) (Concluded)

Figure A-3 (Continued).



(d) 2 September 1977

Figure A-3 (Continued).



1100 - 1200 CST

1400 - 1500 CST

(d) (Concluded)

Figure A-3 (Concluded).

recorded 0.16 ppm ozone levels from 1100 to 1500 CDT, but the three other city stations, Mohawk, health department, and Post office, did not measure ozone levels above 0.10 ppm for these hours. We attempted to adjust the windfield to reflect the observed ozone concentrations by adding data along the sides of the region and modifying some of the wind observations. We received a copy of the strip chart recorded at the Tulsa health department and used these raw data to adjust the downtown wind data. The strip chart pointed out that the wind direction, if automatically averaged, appears to vary rapidly between 20° and 340°, but the reported hourly average was about 180°. As a result, we modified the wind direction in the city area to be reflective of the strip chart recording. Examples of the wind field throughout this day are shown in figure A-3(b).

For the 3 August 1977 simulation two changes were made to wind data. The data collected at Liberty Mounds were not used to prepare the wind file for this day because the wind measurements at Liberty Mounds were inconsistent with the other measurements and because the wind direction monitor was inoperative from 1300 to 1800 CDT. The other change made to the data was the subjective specification of wind data at six additional locations for the hours between 0800 and 1400 CDT. During these hours the windfield was quite changeable; for example, in this time period, the monitor in downtown Tulsa observed a 360° turning of the wind. We used the surface wind data plus the three-hour surface weather maps to construct possible flow patterns for each hour. The synthetic data were added so that the final interpolated windfield would follow the observed patterns. Figure A-3(c) gives examples of the wind field for this day.

The winds were primarily from the south on 2 September 1977. During the middle of the day similar wind directions were observed at all of the sites, but the wind speeds at Liberty Mounds and Ochelata were much lower than those measured at health department and Wynona. We increased the wind speeds at Liberty Mounds and Ochelata to match the speeds at the other two monitoring sites, though this had little effect on the model predictions. Some modifications were also made to the wind directions reported at Ochelata in midafternoon.

At about 1500 the winds shifted from southerly to southeasterly at the health department and Wynona sites. Southwesterly directions reported at Ochelata at this time considerably influenced the calculated flow patterns north of the city. Although the air quality data suggest that pollutants were carried to the Skiatook and Wynona areas in midafternoon, the wind directions calculated using the measured directions at Ochelata yielded wind inputs with a southerly orientation (the southeasterly winds at Wynona countered by southwesterly winds at Ochelata). Therefore, we modified the directions at Ochelata after 1500 CDT to be more consistent with those measured at the health department and Wynona. The wind field for selected hours on this day are shown in figure A-3(d).

The Oklahoma City rawinsondes and the Tulsa pibals on selected days were the basis for estimating wind shear. Since the upper-air data were sparse, a relatively simple algorithm was used for calculating the winds aloft. Winds aloft usually show less spatial variation than do surface winds and are more reflective of the larger-scale synoptic conditions. Therefore, the spatial variations exhibited in the surface winds were decreased with height, which resulted in relatively uniform wind velocities aloft, reflective of the data taken from the rawinsonde measurements.

For the hours between rawinsondes, the winds aloft were averaged from the rawinsonde measurements closest in time. An examination of the limited pibal data gathered in Tulsa and the corresponding rawinsonde data collected in Oklahoma City indicates that the wind direction in Tulsa was about 20° different (in a clockwise direction) from that in Oklahoma City. Thus, for days when no upper-air data were reported for Tulsa (21 July, 29 July, and 3 August), we employed the Oklahoma City data and rotated the wind by 20° in a clockwise direction. Since pibals were released in Tulsa at 0640 and 1035 CDT on 2 September, we employed these data without modification in the specification of winds aloft.

Figures A-3(a) through A-3(d) include the average wind for each level. This gives some idea of the wind shear resulting from the application of this methodology.

The Mixing Height

The height of the inversion base for the modeling days was estimated using the rawinsondes taken twice daily at Oklahoma City and the measured surface temperatures at the airport in Tulsa. For the 2 September simulation, we employed the morning and afternoon aircraft spirals to establish the vertical temperature profile in the Tulsa area. The rawinsondes were released at 0700 and 1900 CDT. For all the modeling days the morning sounding indicated a surface or near-surface inversion, and the afternoon sounding indicated that the inversion had broken up within the lowest 1000 m of the atmosphere. The one exception to this was the 21 July sounding. On this day cloud cover in the afternoon caused the mixing height to rise to only 800 m above ground.

To estimate the mixing depth between the two rawinsondes, we extrapolated the surface temperature at the Tulsa airport upward at the adiabatic lapse rate until it intersected the measured vertical temperature profile. In cases for which the temperature at a particular height differed significantly between the morning and afternoon soundings, we employed a straightforward linear interpolation (in time) to establish suitable temperature profiles throughout the day. These adjustments were made to reflect atmospheric heating and cooling effects. An example of the mixing depth estimation procedure is shown in figure A-4 for 21 July. The diurnal variations of the mixing depth for each modeling day are shown in figures A-5(a) through A-5(d).

The mixing depth was kept spatially constant over the entire modeling region. However, the minimum mixing height was set at 100 m for the city and at 50 m for the rest of the grid to account for the heat island effect and the increased mixing expected in the more populated sections of the modeling region. No other spatial variation was included because we lacked data and physical features that would suggest spatial differences in the height of the mixed layer.

Other Meteorological Inputs

Six meteorological scalars that vary in time only are required as inputs to the SAI Airshed Model. Information needed to calculate each scalar is contained in the routinely collected meteorological data. In this study, the temperature gradient above and below the inversion was calculated from the rawinsonde data. The concentration of water vapor was calculated from humidity data collected at the Tulsa International Airport by the National Weather Service. The atmospheric pressure was set to the nominal value for this area.

The NO_2 photolysis rate constant was based on the solar radiation data collected at Skiatook using the equation $k_1 = 0.4 \times$ solar radiation (in langleys) (Jeffries, Fox, and Kamens, 1975). This formula does not consider the attenuation of solar radiation with height due to light scattering from aerosols. The airshed model does calculate this attenuation when aerosols are simulated, as in the 2 September simulation. Since the aerosol concentrations calculated for the 2 September run were not high, the variation of the photolysis rate with height was not considered significant. We do not expect higher calculated aerosol concentrations from the model simulations for the other days. Thus, ignoring the attenuation for the other days is expected to have had little effect on the model predictions.

One adjustment was made to the above methodology for specifying the photolysis rate constants. At 1600 CDT on 21 July the solar radiation measured at Skiatook fell to near-zero levels due to cloud cover. Examination of the NO_x and O_3 data collected during the afternoon of 21 July suggests that photochemical reactions did not stop at 1600 CDT or even an

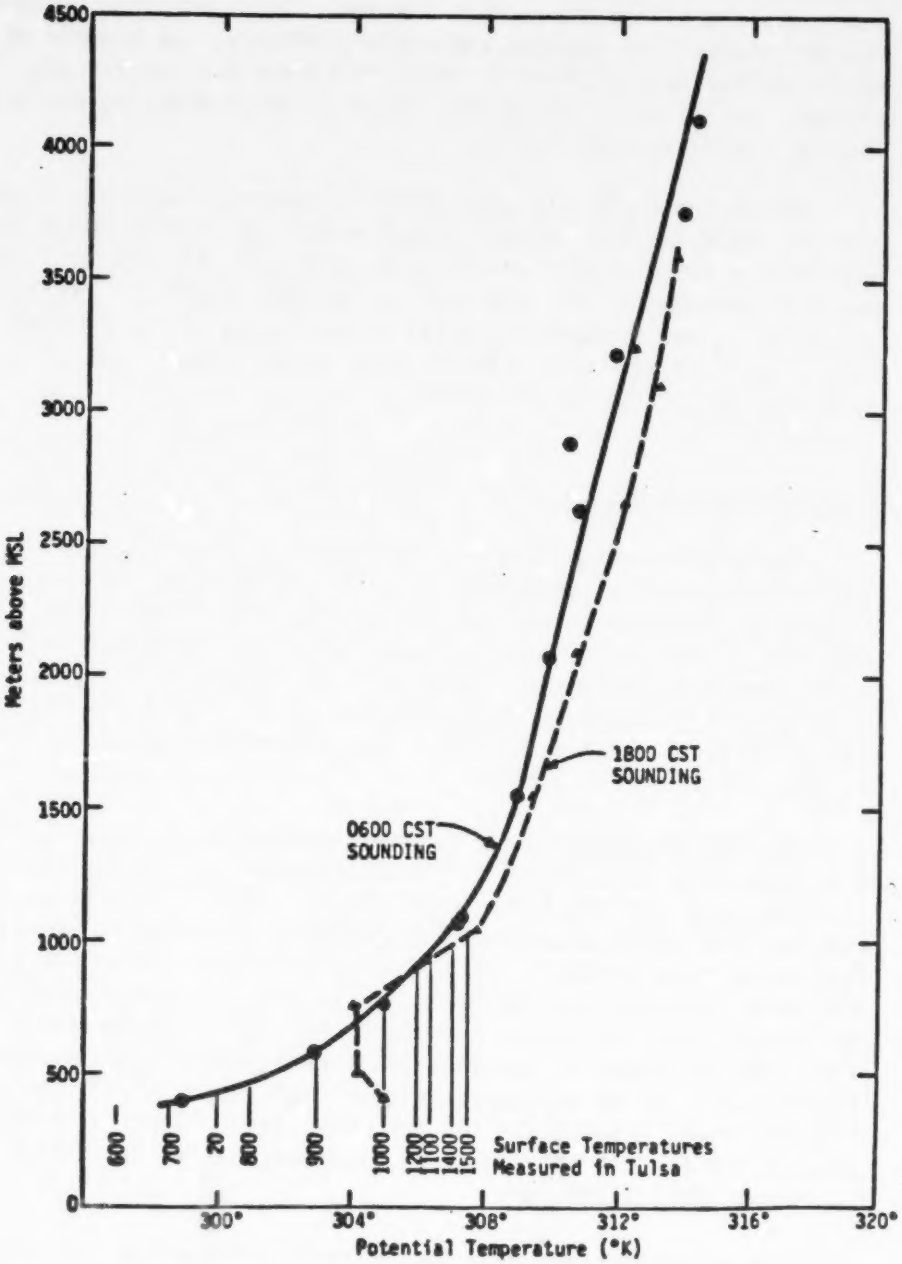
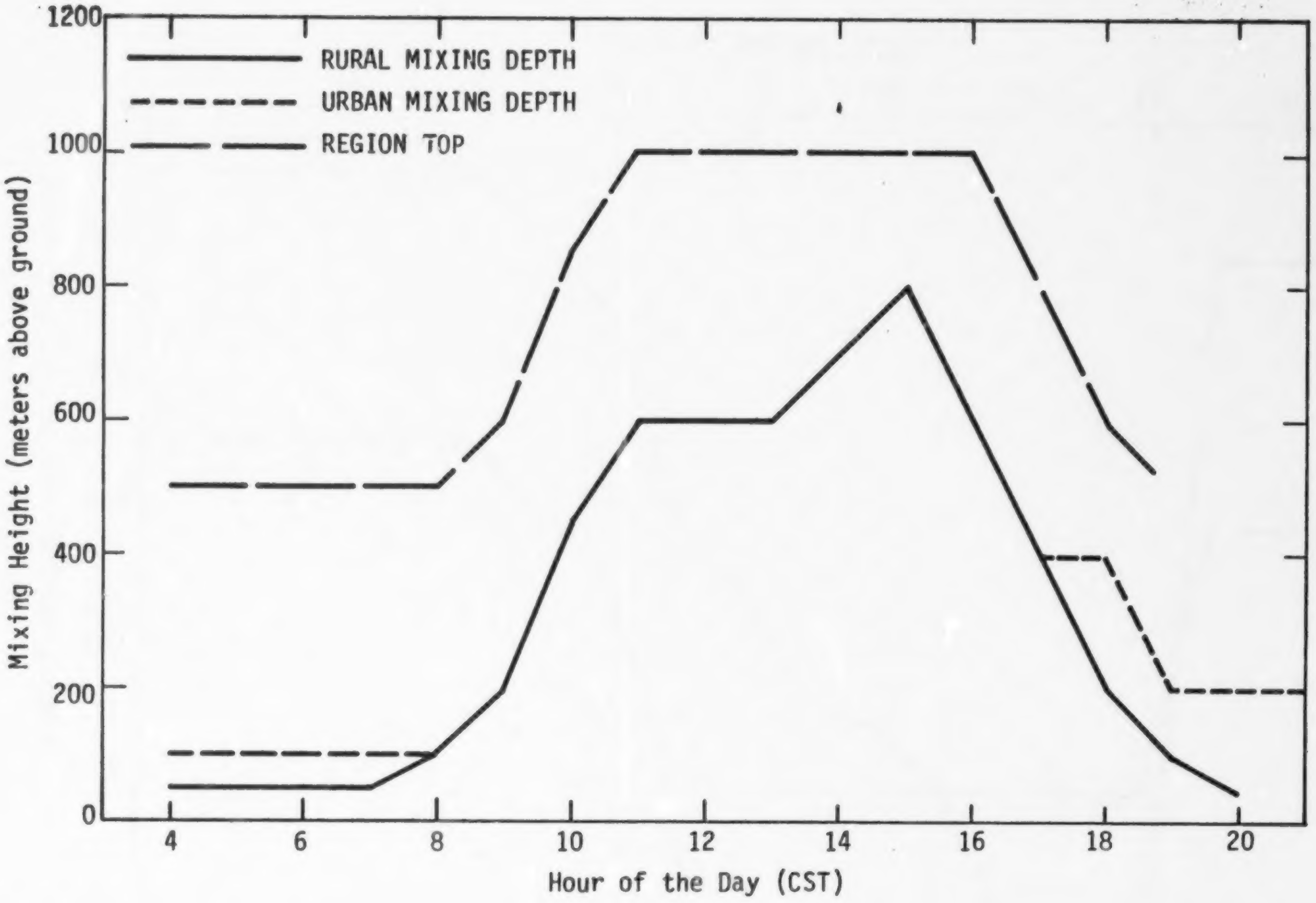


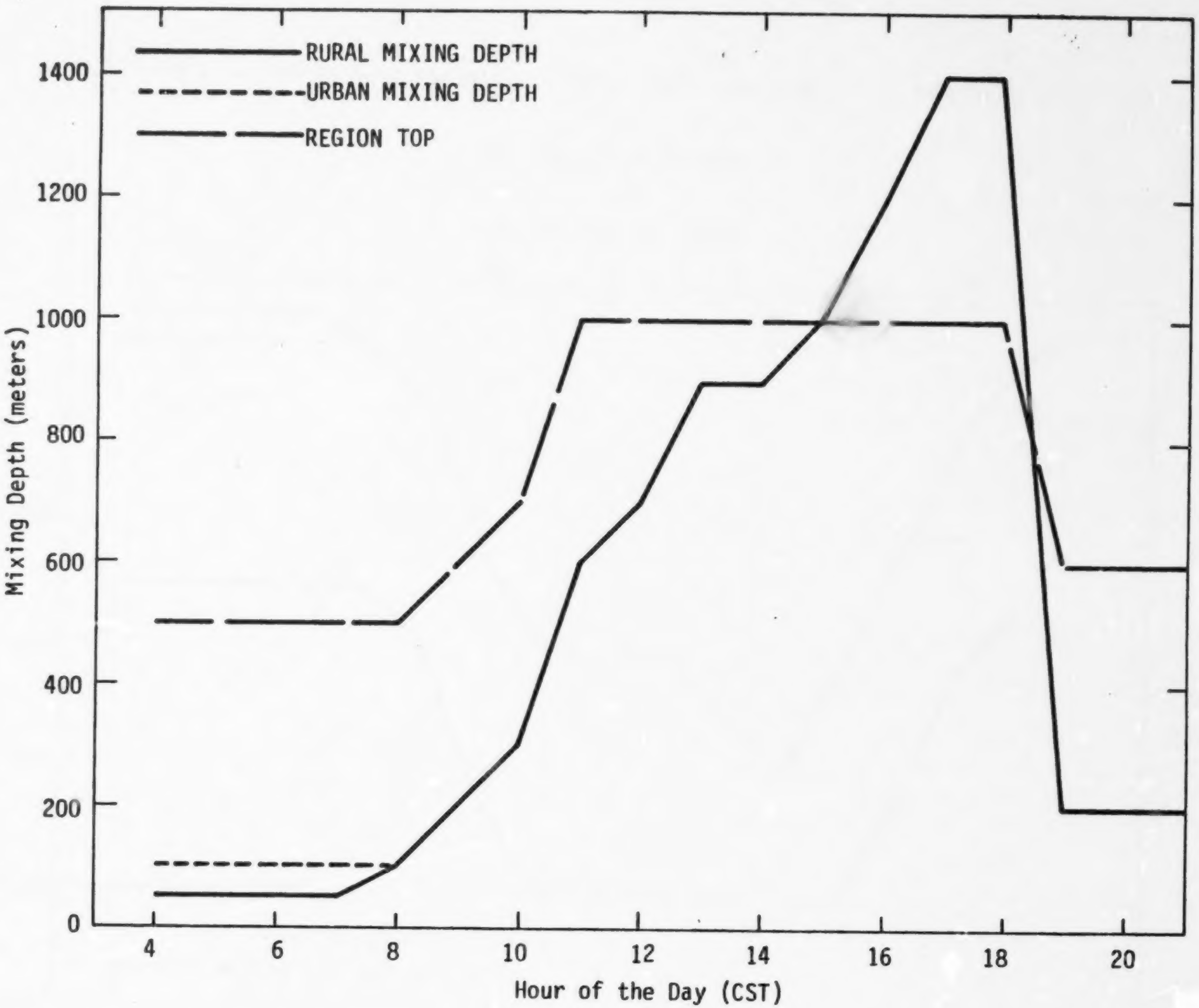
Figure A-4. Temperature soundings in Oklahoma City and Tulsa surface temperatures for 21 July 1977.

49r 81 18



(a) For 21 July 1977

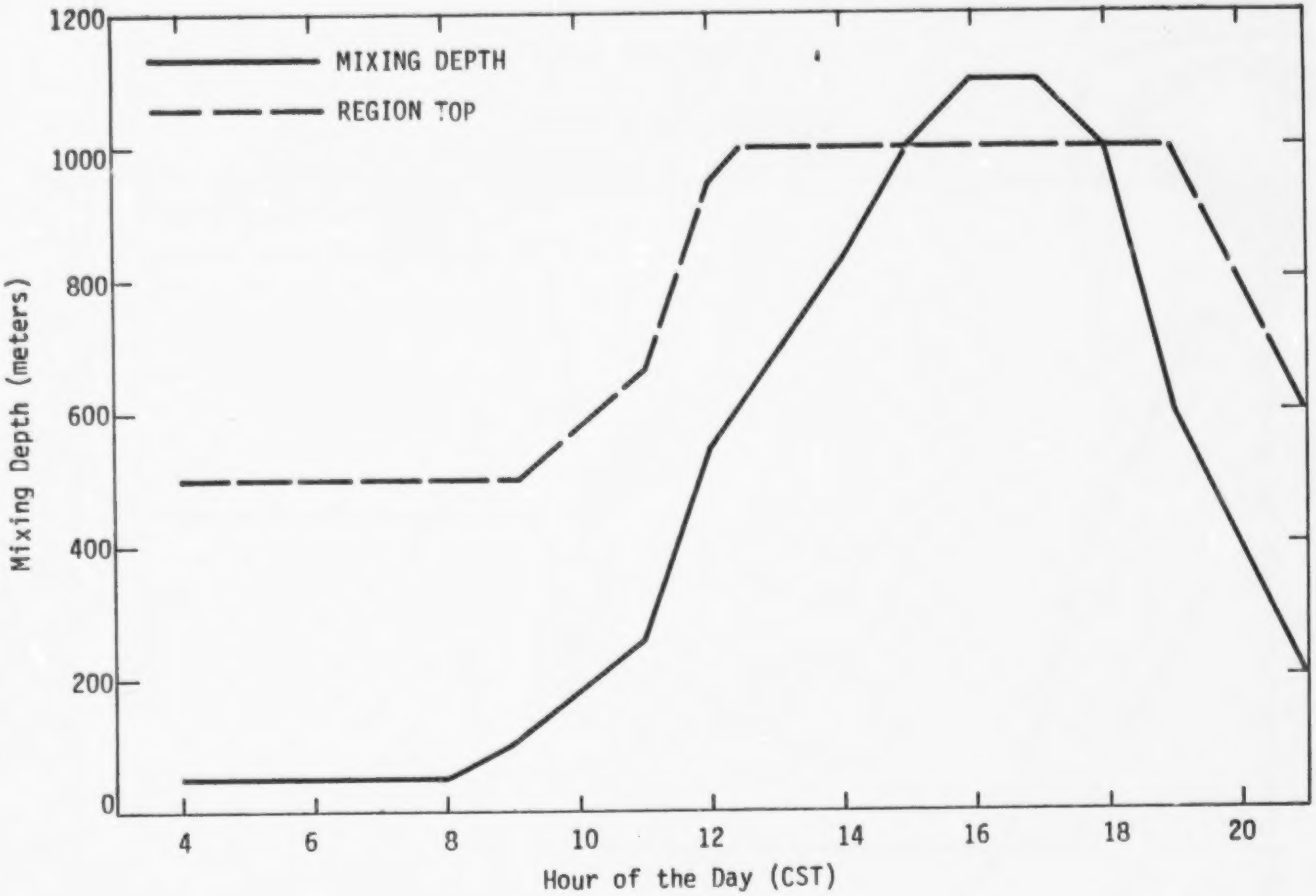
Figure A-5. The diurnal pattern of the mixing depth and top of the modeling region



(b) For 29 July 1977

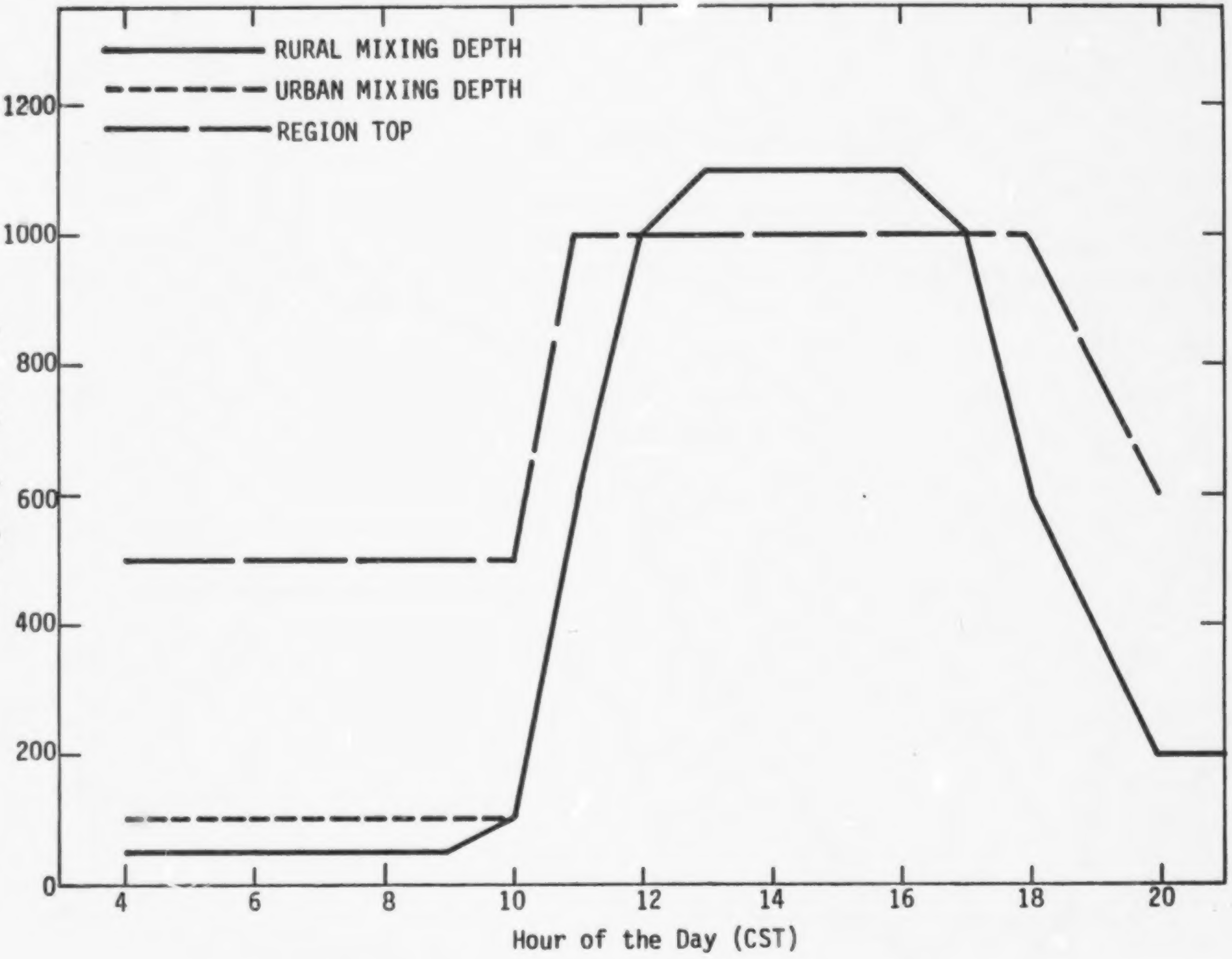
Figure A-5 (Continued).

49r 81 18



(c) 3 August 1977

Figure A-5 (Continued).



(d) For 2 September 1977

Figure A-5 (Concluded).

hour or two later. Upon review of the surface wind data, we found that the wind directions reported at Wynona, Ochelata, and health department shifted from a southerly to westerly or northwesterly orientation at 1500, 1700, and 1800 CDT, respectively. Since the drop in solar radiation measured in the northwestern portion of the modeling region seemed to be correlated with the shift in the surface wind directions, we suspected that the solar radiation might not have been spatially uniform over the modeling region. To account for the observed ozone, we averaged the 21 July solar radiation data with the data taken on the next sunny day.

The following tablulation was used to estimate the exposure class, which was also based on the solar radiation data:

Solar Radiation (langleys)	Exposure Class
0. - 0.25	0
0.25 - 0.75	1
0.75 - 1.25	2
> 1.25	3

The last meteorological input is the surface temperature, which was set spatially constant for the entire region based on the hourly values measured at the Tulsa airport. These values and the hourly values for the other meteorological variables for each day are summarized in table A-5.

EMISSIONS INPUTS

The EPA contracted with Engineering-Science to develop a complete emissions inventory for the Tulsa area. The only modification we made to this inventory was to double the grid spacing.

Two issues were raised during this project concerning changes to the emissions inventory. One was the differences in mobile sources on Fridays. The other involved possible changes in the reactivity of perchloroethylene. Two of the modeling days, 2 September and 29 July 1977, were Fridays. We discussed the difference between average weekday and Friday emissions with Mr. Jerry Howell of the Indian Nations Council of Governments (INCOG). We concluded that mobile source emissions on Friday might be from 10 to 15 percent greater than those on average weekdays, but there were few data available to quantify any spatial or temporal changes to the emissions inventory. Since the uncertainty in the complete emissions inventory is likely to be at least as great as any proposed change, we decided to make no modifications to the inventory.

49Γ 81 10

TABLE A-5. VALUES OF METEOROLOGICAL SCALARS

(a) For 21 July 1977

Time (CST)	NO_2 Photolysis Rate Constant (min^{-1})	Exposure Class	Temperature Gradient above Mixed Layer (°C/m)	Temperature Gradient in Mixed Layer (°C/m)	Water Concentration (ppm)	Temperature (°C)
0400	0.0	0	-0.0036	-0.01	25,000	24
0500	0.016	0	-0.0036	-0.01	25,000	24
0600	0.080	1	-0.0036	-0.01	25,000	26
0700	0.190	1	-0.0036	-0.01	25,000	28
0800	0.300	2	-0.0036	-0.01	25,000	30
0900	0.43	2	-0.0036	-0.01	28,000	32
1000	0.50	3	-0.0036	-0.01	29,000	33
1100	0.51	3	-0.0036	-0.01	30,000	33
1200	0.48	3	-0.0036	-0.01	30,000	33
1300	0.50	3	-0.0036	-0.01	30,000	34
1400	0.38	2	-0.0036	-0.01	28,000	34
1500	0.21	1	-0.0036	-0.01	25,000	32
1600	0.15	1	-0.0036	-0.01	25,000	29
1700	0.09	0	-0.0036	-0.01	25,000	28
1800	0.01	0	-0.0036	-0.01	26,000	28
1900	0.0	0	-0.0036	-0.01	27,000	27
2000	0.0	0	-0.0036	-0.01	27,000	27

49Г 81 10

TABLE A-5 (Continued)

(b) For 29 July 1977

Time (CST)	NO_2 Photolysis Rate Constant (min^{-1})	Exposure Class	Temperature Gradient above Mixed Layer (°C/m)	Temperature Gradient in Mixed Layer (°C/m)	Water Concentration (ppm)	Temperature (°C)
0400	0.0	0	-0.005	-0.01	27,000	24
0500	0.004	0	-0.005	-0.01	27,000	23
0600	0.056	1	-0.005	-0.01	27,000	23
0700	0.17	1	-0.005	-0.01	29,000	25
0800	0.28	2	-0.005	-0.01	29,000	27
0900	0.37	2	-0.005	-0.01	30,000	29
1000	0.44	3	-0.005	-0.01	30,000	29
1100	0.40	3	-0.005	-0.01	30,000	31
1200	0.45	3	-0.005	-0.01	29,000	32
1300	0.49	3	-0.005	-0.01	28,000	33
1400	0.30	2	-0.005	-0.01	27,000	32
1500	0.37	2	-0.005	-0.01	27,000	33
1600	0.29	2	-0.005	-0.01	25,000	34
1700	0.19	1	-0.005	-0.01	25,000	34
1800	0.064	0	-0.005	-0.01	24,000	34
1900	0.008	0	-0.005	-0.01	27,000	32
2000	0.0	0	-0.005	-0.01	27,000	31

TABLE A-5 (Continued)

(c) For 3 August 1977

Time (CST)	NO_2 Photolysis Rate Constant (min^{-1})	Exposure Class	Temperature Gradient above Mixed Layer (°C/m)	Temperature Gradient in Mixed Layer (°C/m)	Water Concentration (ppm)	Temperature (°C)
0400	0.	0	0.0025	-0.01	23,000	23
0500	0.008	0	0.0025	-0.01	23,000	23
0600	0.032	0	0.0025	-0.01	23,000	23
0700	0.120	1	0.0025	-0.01	24,000	26
0800	0.200	1	0.0025	-0.01	25,000	29
0900	0.128	1	0.0025	-0.01	23,000	28
1000	0.328	2	0.0025	-0.01	26,000	28
1100	0.544	3	0.0025	-0.01	23,000	31
1200	0.564	3	0.0025	-0.01	23,000	33
1300	0.536	3	0.0025	-0.01	24,000	33
1400	0.488	3	0.0025	-0.01	23,000	35
1500	0.404	3	0.0025	-0.01	22,000	34
1600	0.304	2	0.0025	-0.01	22,000	35
1700	0.168	1	0.0025	-0.01	20,000	34
1800	0.040	0	-0.01	0.0	23,000	34
1900	0.004	0	-0.01	0.0	23,000	31
2000	0.0	0	-0.01	0.0	23,000	29

49r 81 10

TABLE A-5 (Concluded)

(d) For 2 September 1977

Time (CST)	NO_2 Photolysis Rate Constant (min^{-1})	Exposure Class	Temperature Gradient above Mixed Layer (°C/m)	Temperature Gradient in Mixed Layer (°C/m)	Water Concentration (ppm)	Temperature (°C)
0400	0.0	0	0.0006	-0.003	24,000	22
0500	0.0	0	0.0006	-0.003	24,000	22
0600	0.040	0	0.0006	-0.003	24,000	23
0700	0.12	1	0.0006	-0.003	26,000	26
0800	0.26	1	0.0006	-0.003	27,000	28
0900	0.33	2	0.0006	-0.003	27,000	29
1000	0.46	2	0.0006	-0.003	26,000	31
1100	0.56	3	0.0006	-0.003	28,000	31
1200	0.52	3	0.0006	-0.003	25,000	32
1300	0.48	2	0.0006	-0.003	22,000	32
1400	0.41	2	0.0006	-0.003	23,000	33
1500	0.25	1	0.0006	-0.003	23,000	33
1600	0.16	1	0.0006	-0.003	22,000	32
1700	0.10	1	0.0006	-0.003	22,000	31
1800	0.020	0	-0.003	-0.003	24,000	28
1900	0.0	0	-0.003	-0.003	23,000	27
2000	0.0	0	-0.003	-0.003	23,000	27

49r 81 10

Perchloroethylene is a solvent widely used in dry cleaning. Engineering-Science considered this compound unreactive when they compiled the Tulsa emissions inventory. After further investigations, we concluded that perchloroethylene is less reactive than propane, which is considered to be half as reactive as the higher-carbon-number paraffins. Emissions from dry cleaning establishments account for less than 5 percent of total hydrocarbon emissions, and since perchloroethylene has a relatively low reactivity, we chose not to alter the reactivity of perchloroethylene. If we had changed the reactivity to the low value, we would anticipate a change in the ozone predictions of no more than a few percent.

Tables A-6(a) through A-6(g) present the total gridded emissions for NO, NO_2 paraffins, olefins, aromatics, ethylenes, and aldehydes for the period from 0100 to 2300 CDT. This is the time period over which the model simulations were conducted.

MISCELLANEOUS INPUTS

Additional inputs required by the SAI Airshed Model include gridded fields of two ground-surface characteristics--surface roughness and a surface deposition factor. The surface roughness is used to calculate the vertical diffusivity coefficient. The surface deposition factor is employed in the calculation of the surface deposition velocity, which is used to estimate the rate of pollutant removal from the atmosphere by the surface uptake processes described earlier in section 5. Since these two variables depend on land use, vegetation, and the types of development found in each grid square, their values can be estimated employing maps that describe land use. U.S. Geological Survey maps having a scale of 1:250,000 for the Tulsa area were useful for this task. In addition, land-use maps prepared by the local planning agency were consulted in developing gridded fields of surface roughness and surface deposition factors. Table A-7 gives the estimates of surface roughness and deposition velocity for each land-use category we considered.

TABLE A-6. TOTAL DAILY EMISSIONS

(tons)

(a) NO

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.04	0.10	0.01	0.00	0.00	0.00	0.00
31	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.03	0.08	0.00	0.00	0.00	0.00	0.00
30	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.00	0.00	0.00	0.00	0.00
29	0.00	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.03	0.06	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.02	0.12	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.06	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.00	0.07	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.06	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.08	0.04	0.05	0.04	0.00	0.00
23	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.26	0.36	0.30	0.07	0.46	0.11	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.12	0.31	0.09	0.43	0.27	0.09	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.23	0.37	0.19	0.58	0.23	0.03	0.00
20	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.48	0.70	0.18	0.89	0.17	0.03	0.00
19	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.15	0.72	0.98	0.69	0.86	0.17	0.16	0.00
18	0.00	0.02	0.01	0.00	0.00	0.02	0.03	0.27	1.38	1.08	1.50	1.57	0.45	0.30	0.00
17	0.00	0.01	0.39	0.36	0.32	1.10	1.58	14.79	6.39	3.52	2.92	2.21	1.07	0.39	0.00
16	0.00	0.11	0.01	0.01	0.11	0.70	0.32	1.42	2.42	2.57	3.61	1.57	0.15	0.13	0.00
15	0.00	0.00	0.01	0.01	0.03	0.14	0.69	1.48	1.47	2.18	1.77	1.12	1.32	0.47	0.00
14	0.00	0.00	0.00	0.00	0.00	0.09	0.19	0.52	0.79	0.50	0.32	0.24	0.60	0.26	0.00
13	0.00	0.00	0.00	0.02	0.09	0.49	0.09	0.46	0.14	0.17	0.37	0.19	0.18	0.05	0.00
12	0.00	0.00	0.02	0.10	0.00	0.10	0.02	0.33	0.04	0.01	0.22	0.10	0.16	0.00	0.00
11	0.00	0.05	0.10	0.05	0.00	0.00	0.06	0.18	0.03	0.04	0.36	0.05	0.06	0.02	0.00
10	0.00	0.07	0.01	0.00	0.00	0.00	0.05	0.14	0.01	0.01	0.02	0.00	0.00	0.00	0.00
9	0.00	0.00	0.01	0.00	0.00	0.00	0.05	0.13	0.00	0.03	0.01	0.00	0.00	0.00	0.00
8	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.01	0.01	0.01	0.02	0.05	0.10	0.08	0.01	0.01	0.01	0.01	0.01	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.16	0.00	0.00	0.01	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.10	0.00	0.01	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.64	0.30	0.01	0.02	0.00	0.00	0.00
2	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.13	0.37	0.05	0.09	0.02	0.01	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE A-6 (Continued)

(b) NO_2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.03	0.01	0.03	0.01	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.05	0.03	0.01	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.02	0.06	0.02	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.07	0.01	0.09	0.02	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.08	0.10	0.08	0.09	0.02	0.02	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.16	0.10	0.13	0.16	0.05	0.03	0.00
17	0.00	0.00	0.04	0.04	0.03	0.10	0.17	0.96	0.62	0.37	0.29	0.23	0.12	0.04	0.00
16	0.00	0.01	0.00	0.00	0.01	0.07	0.03	0.15	0.21	0.26	0.37	0.17	0.02	0.01	0.00
15	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.16	0.15	0.23	0.19	0.12	0.14	0.08	0.00
14	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.06	0.09	0.03	0.04	0.03	0.06	0.03	0.00
13	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.03	0.02	0.02	0.04	0.02	0.02	0.01	0.00
12	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.04	0.00	0.00	0.02	0.01	0.02	0.00	0.00
11	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.04	0.01	0.01	0.00	0.00
10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.00	0.01	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE A-6 (Continued)

(c) Parafins

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.03	0.06	0.16	0.05	0.09	0.02	0.00	0.00
31	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.02	0.07	0.04	0.01	0.02	0.00	0.00
30	0.00	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.06	0.04	0.01	0.01	0.00	0.00
29	0.00	0.02	0.02	0.02	0.03	0.02	0.01	0.03	0.02	0.06	0.01	0.01	0.01	0.00	0.00
28	0.00	0.02	0.01	0.02	0.35	0.03	0.03	0.04	0.01	0.09	0.01	0.00	0.01	0.00	0.00
27	0.00	0.01	0.02	0.01	0.01	0.01	0.03	0.02	0.00	0.01	0.06	0.01	0.01	0.00	0.00
26	0.00	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.00	0.01	0.06	0.01	0.01	0.00	0.00
25	0.00	0.01	0.00	0.02	0.01	0.01	0.00	0.02	0.01	0.02	0.05	0.01	0.01	0.00	0.00
24	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.03	0.05	0.05	0.06	0.06	0.00	0.00
23	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.25	0.23	0.23	0.09	0.24	0.03	0.00	0.00
22	0.00	0.00	0.03	0.01	0.01	0.00	0.01	0.04	0.11	0.24	0.07	0.20	0.07	0.01	0.00
21	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.05	0.21	0.31	0.22	0.30	0.05	0.01	0.00
20	0.00	0.01	0.02	0.00	0.01	0.01	0.05	0.04	0.38	0.44	0.17	0.47	0.06	0.03	0.00
19	0.00	0.03	0.02	0.01	0.01	0.01	0.03	0.23	1.00	0.71	0.53	0.58	0.08	0.09	0.00
18	0.00	0.05	0.02	0.01	0.01	0.01	0.04	0.28	1.91	1.34	1.87	1.18	0.18	0.16	0.00
17	0.00	0.04	0.29	0.21	0.19	1.83	1.10	41.41	6.22	4.13	3.12	2.32	0.66	0.24	0.00
16	0.00	0.13	0.02	0.03	0.13	0.48	0.27	2.19	25.27	3.30	4.49	1.56	0.06	0.05	0.00
15	0.00	0.10	0.03	0.02	0.04	0.14	0.56	1.14	1.77	2.32	1.60	0.81	0.96	0.28	0.00
14	0.00	0.02	0.02	0.01	0.02	0.09	0.19	0.30	0.22	0.43	0.30	0.11	0.51	0.16	0.00
13	0.00	0.01	0.01	0.03	0.07	0.54	0.09	0.31	0.87	0.11	0.24	0.09	0.13	0.03	0.00
12	0.00	0.03	0.02	0.09	0.01	0.11	0.16	1.58	0.58	0.03	0.17	0.05	0.07	0.01	0.00
11	0.00	0.06	0.08	0.06	0.01	0.01	0.06	0.15	0.05	0.05	0.20	0.05	0.06	0.02	0.00
10	0.00	0.06	0.01	0.01	0.01	0.01	2.97	0.08	0.02	0.02	0.03	0.01	0.01	0.01	0.00
9	0.00	0.01	0.02	0.01	0.01	0.01	0.03	0.09	0.01	0.05	0.01	0.01	0.01	0.00	0.00
8	0.00	0.02	0.04	0.01	0.01	0.02	0.03	0.08	0.01	0.01	0.00	0.01	0.01	0.00	0.00
7	0.00	0.01	0.05	0.01	0.01	0.01	0.02	0.08	0.01	0.01	0.01	0.02	0.01	0.00	0.00
6	0.00	0.01	0.02	0.02	0.02	0.02	0.05	0.07	0.06	0.02	0.02	0.02	0.03	0.01	0.00
5	0.00	0.01	0.01	0.01	0.01	0.01	0.94	0.01	0.11	0.02	0.01	0.02	0.04	0.01	0.00
4	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.05	0.08	0.01	0.03	0.01	0.01	0.00
3	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	8.98	0.21	0.01	0.03	0.02	0.01	0.00
2	0.00	0.01	0.01	0.02	0.01	0.01	0.02	0.02	0.10	0.20	0.05	0.10	0.03	0.01	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

49r 81 18

TABLE A-6 (Continued)

(d) Olefins

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.01	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.02	0.01	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.01	0.04	0.01	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.06	0.04	0.05	0.01	0.01	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.13	0.08	0.11	0.08	0.01	0.01	0.00
17	0.00	0.00	0.03	0.02	0.01	0.08	0.08	1.15	0.41	0.29	0.21	0.16	0.05	0.02	0.00
16	0.00	0.01	0.00	0.00	0.01	0.03	0.02	0.11	0.77	0.23	0.32	0.11	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.09	0.12	0.16	0.11	0.06	0.07	0.02	0.00
14	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.01	0.03	0.02	0.01	0.03	0.01	0.00
13	0.00	0.00	0.00	0.00	0.01	0.04	0.00	0.02	0.02	0.01	0.02	0.01	0.01	0.00	0.00
12	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.03	0.00	0.00	0.01	0.00	0.01	0.00	0.00
11	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00
10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.02	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

49r 81 18

TABLE A-6 (Continued)

(e) Aromatics

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.03	0.01	0.03	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.03	0.01	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.03	0.04	0.01	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.05	0.02	0.06	0.01	0.00	0.00
19	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.13	0.09	0.07	0.08	0.01	0.01	0.00
18	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.03	0.23	0.17	0.39	0.16	0.32	0.58	0.00
17	0.00	0.00	0.04	0.02	0.02	0.39	0.14	7.19	0.73	0.52	0.39	0.32	0.09	0.03	0.00
16	0.00	0.01	0.00	0.00	0.01	0.06	0.04	0.35	5.06	0.43	0.38	0.20	0.01	0.01	0.00
15	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.15	0.23	0.30	0.21	0.10	0.12	0.04	0.00
14	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.04	0.03	0.05	0.04	0.01	0.06	0.02	0.00
13	0.00	0.00	0.00	0.00	0.01	0.07	0.01	0.03	0.09	0.01	0.03	0.01	0.02	0.30	0.00
12	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.11	0.01	0.00	0.02	0.01	0.01	0.00	0.00
11	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.02	0.00	0.01	0.00	0.00
10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.64	0.03	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.01	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4yr 81 18

TABLE A-6 (Continued)

(f) Ethylene

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.02	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.01	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.02	0.01	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.01	0.04	0.01	0.00	0.00
19	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.02	0.06	0.04	0.02	0.05	0.01	0.01	0.00
18	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.03	0.13	0.07	0.09	0.08	0.02	0.02	0.00
17	0.00	0.00	0.03	0.02	0.02	0.28	0.09	0.28	0.45	0.30	0.21	0.16	0.06	0.02	0.00
16	0.00	0.01	0.00	0.00	0.01	0.04	0.02	0.09	0.12	0.23	0.33	0.11	0.01	0.01	0.00
15	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.09	0.11	0.17	0.11	0.07	0.08	0.03	0.00
14	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.02	0.03	0.02	0.01	0.03	0.01	0.00
13	0.00	0.00	0.00	0.00	0.01	0.03	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.00	0.00
12	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.00	0.01	0.01	0.01	0.00	0.00
11	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.02	0.00	0.01	0.00	0.00
10	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE A-6 (Continued)

(g) Aldehydes

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.03	0.02	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.04	0.11	0.04	0.01	0.01	0.00
17	0.00	0.00	0.01	0.01	0.01	0.21	0.03	0.10	0.23	0.11	0.08	0.06	0.02	0.01	0.00
16	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.04	0.06	0.09	0.13	0.04	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.04	0.07	0.05	0.03	0.03	0.01	0.00
14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.00
13	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30	0.01	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE A-7. SURFACE AND VEGETATION FACTORS BY LAND USE CATEGORY

Land Use Category	Surface Roughness (m)	Vegetation Factors*
Woods-brushwood	2.0	2.0
Grass or crops	0.1	1.0
General urban	0.7	0.5
Residential	0.5	1.0
Commercial	0.5	0.2
Central business district	3.0	0.2
Industrial	1.0	0.2
Parks	1.2	1.0
Water	0.002	4.0

Source: Sellers (1965).

* The vegetation factors are dimensionless and represent the pollutant uptake effectiveness of a particular type of land use (or vegetation cover) relative to that of alfalfa.

49r 81 10